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Electrochemical methods for synthesis of organometallic compounds

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Abstract:	The electrochemical methods have a huge synthetic potential in both academia and industry. However, the implementation of electrochemistry for the synthesis of organometallic compounds is presented limitedly, while the sustainability and greenness of the electrochemical protocols allow considering them as a very promising and intriguing approach. This review summarizes the most important and practically useful advances in the electrochemistry of organometallics with the emphases on the direct electrochemical synthesis of organometallic derivatives by the formation of a carbon-metal bond, electrosynthesis of organic compounds mediated by in situ generated organometallics as well as cyclic voltammetry and related methods, applied for analysis and preparation of organometallic compounds.
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	Alexander Trifonov, Prof. Dr. Director, Institute of Metal-Organic Chemistry named after Razuvaev Russian Academy of Sciences: FGBUN Institut metalloorganiceskoj himii im G A Razuvaeva Rossijskoj akademii nauk trif@iomc.ras.ru Prof. Dr. Alexander Trifonov is an expert in synthetic chemistry of organoelement compounds, including organometallics, and homogeneous catalysis.
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Dear Prof. Philip Gale,

attached please find the manuscript “Electrochemical methods for synthesis of organometallic compounds” by the authors: Zufar N. Gafurov, Artyom O. Kantyukov, Alexey A. Kagilev, Oleg G. Sinyashin and Dmitry G. Yakhvarov, prepared for publication in COORDINATION CHEMISTRY REVIEWS.

Currently the electrochemical methods have a huge synthetic potential in both academia and industry. However, the synthetic application for preparation of organometallic compounds is relatively rare while the electrochemical methods have a lot of advance in comparison to the classical procedures like mild conditions, the use of non-flammable solvents, absence of the by-products etc. Moreover, the electrochemical methods operate in ecologically safe conditions according to the main principals of “green chemistry”. In this context the elaboration of new synthetic procedures for the preparation of organometallic compounds is of high interest. This review summarizes the most important and practically useful advances in the electrochemistry of organometallics with the emphases on the direct electrochemical synthesis of organometallic derivatives by the formation of a carbon-metal bond, electrosynthesis of organic compounds mediated by in situ generated organometallics as well as cyclic voltammetry and related methods, applied for analysis and investigation of the structure of organometallic compounds formed in situ. The review contains 225 references described modern results of developing of this research topic.

Thus, in view of prompt publication of this important for world scientific community materials, we submit this review to a special issue of ICCC-2021 (Part 1) of the COORDINATION CHEMISTRY REVIEWS as an international journal presenting review accounts of original and significant results in coordination chemistry.

To further acquaint you with the specifics of this research topic we are submitting the final draft of this review via on-line platform. I hope you will consider this manuscript suitable for publication in this special issue of this high-quality journal. I look forward to your reply and comments of the referee concerning the topic and quality of this manuscript. Many thanks in advance.

I am looking forward to hearing from you soon!

Sincerely,
Dmitry Yakhvarov

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Highlights.

► Electrochemical methods have been used for the preparation of organometallic compounds. ► Main electrochemical synthetic and analytical methods and types of the electrochemical cells are described. ► The electrochemically generated high-reactive organometallic species have been used *in situ* as the reagents for the synthesis of organic and organoelement compounds. ► The application of *in situ* spectroelectrochemical methods for elucidating of the nature of organometallic intermediates formed in the electrochemical process and their application for the activation of organometallics for catalytical purposes are discussed.

Graphical Abstract

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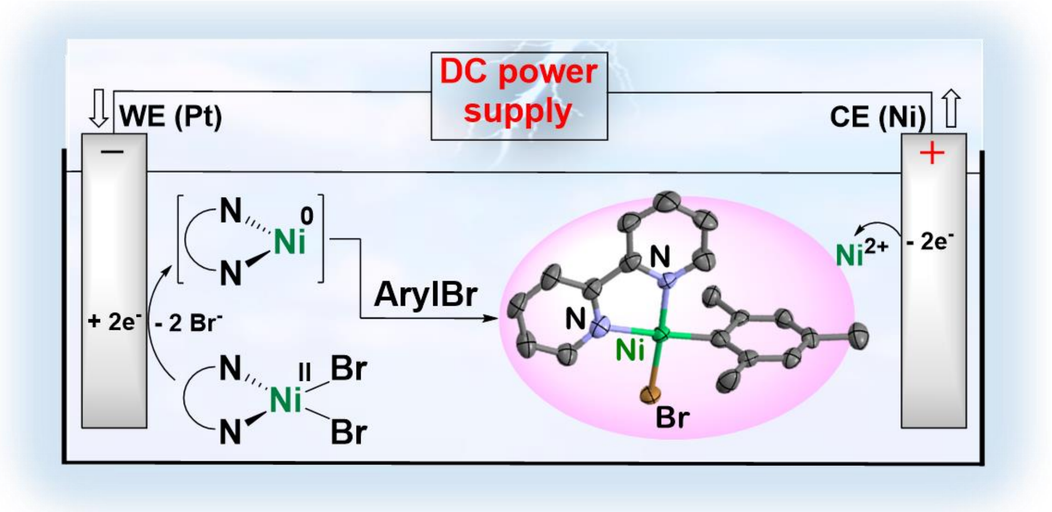
Graphical abstract



Electrochemical methods for synthesis of organometallic compounds

Zufar N. Gafurov[a,*], Artyom O. Kantyukov[a,b], Alexey A. Kagilev[a,b], Oleg G. Sinyashin[a], Dmitry G. Yakhvarov[a,b,*]

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Abstract

The electrochemical methods have a huge synthetic potential in both academia and industry. However, the implementation of electrochemistry for the synthesis of organometallic compounds is presented limitedly, while the sustainability and greenness of the electrochemical protocols allow considering them as a very promising and intriguing approach. This review summarizes the most important and practically useful advances in the electrochemistry of organometallics with the emphases on the direct electrochemical synthesis of organometallic derivatives by the formation of a carbon-metal bond, electrosynthesis of organic compounds mediated by *in situ* generated organometallics as well as cyclic voltammetry and related methods, applied for analysis and preparation of organometallic compounds.

Keywords: electrochemistry; cyclic voltammetry; electrochemical activation; electrosynthesis; organometallic compounds; high-reactive intermediates; electrocatalysis.

Abbreviations: AC, alternating current; bpy, 2,2'-bipyridine; CE, counter electrode; Cp, cyclopentadienyl; CV, cyclic voltammetry; DC, direct current; Dipp, 2,6-diisopropylphenyl; dmbpy, 4,4′-dimethoxy-2,2′-bipyridine; dme, dimethoxyethane; dppe, bis(diphenylphosphino)ethane; dtbbpy, 4,4′-di-tert-butyl-2,2′-bipyridine; eapt, (2Z)-2-[(2-hydroxyethyl)imino]-3-allyl-1,3-thiazolidin-4-one; HFI, hyperfine interaction; HMPA, hexamethylphosphoramide; Mes, 2,4,6-trimethylphenyl; MPzCl, 4-(6-chloropyridazin-3-yl)morpholine; NHP, *N*-hydroxyphthalimide; papt, (2Z)-2-(phenylimino)-3-allyl-1,3-thiazolidin-4-one; Py, pyridine; RE, reference electrode; RVC, reticulated vitreous carbon; SCE, saturated calomel electrode; SEC, spectroelectrochemistry; SHE, standard hydrogen electrode; Tchp, 2,4,6-tricyclohexylphenyl; TFE, trifluoroethanol; Tipp, 2,4,6-triisopropylphenyl; TMSCl, trimethylsilyl chloride; WE, working electrode; Xyl, 2,6-dimethylphenyl.

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1. Introduction

Electrochemical techniques have a wide range of application moving from lab-scale use to industrial production processes [1–8]. These techniques are quite diverse and usually divided to anodic, cathodic or paired electrolysis, including direct or mediated processes, applying divided or undivided electrochemical cells (Figure 1-A and B), under galvanostatic (applying a constant current density) or potentiostatic (maintaining a constant potential at the working electrode) conditions [9–16]. However, all these methods are based on the same principle: addition or removal of electrons from substrate through the direct application of an electrical potential. The common setup of the electrochemical cell [16–19] includes a direct current (DC) power supply, connected to two oppositely charged electrodes, immersed to the reaction mixture (Figure 1-C). The electrode, which is responsible for electron transfer to or from the substrate molecule is so-called *working electrode (WE)*; while the opposite one – *counter electrode (CE)* – is responsible for the electron balance performed by counter process. Moreover, *reference electrode (RE)* may be applied for the control of the potential of the *working electrode*. The electrode for reducing of the substrate molecule is considered as *cathode*, while oxidation of the substrate is carried out on the *anode*. The nature of the counter process is the function of the *counter electrode* charge, for anode as CE the oxidation of a solvent, electrolyte or material of the electrode (in case of a sacrificial metal anode where the oxidative dissolution of anode *e.g.*, Mg, Zn, or Fe takes place) (see Figure 1-C, positions a-d). However, most of chemists are used to ignore the counter RedOx processes (see Figure 1-C, positions 2, 3 and 4) unless they do not affect to the target interaction and the product formation. If so, the separation of the electrode compartments (*anolyte* and *catholyte*) is used by adding a diaphragm (or a salt bridge) between them (see Figure 1-C, position 1), which prevents the undesirable mixing of anolyte and catholyte solutions. Such a system is known as *divided electrochemical cell*. Nevertheless, there are also known so-called paired electrolysis (see Figure 1-

C, position iii), where both anodic and cathodic processes are necessary for generation of the target product, in this case the *undivided electrochemical cell* is applied.

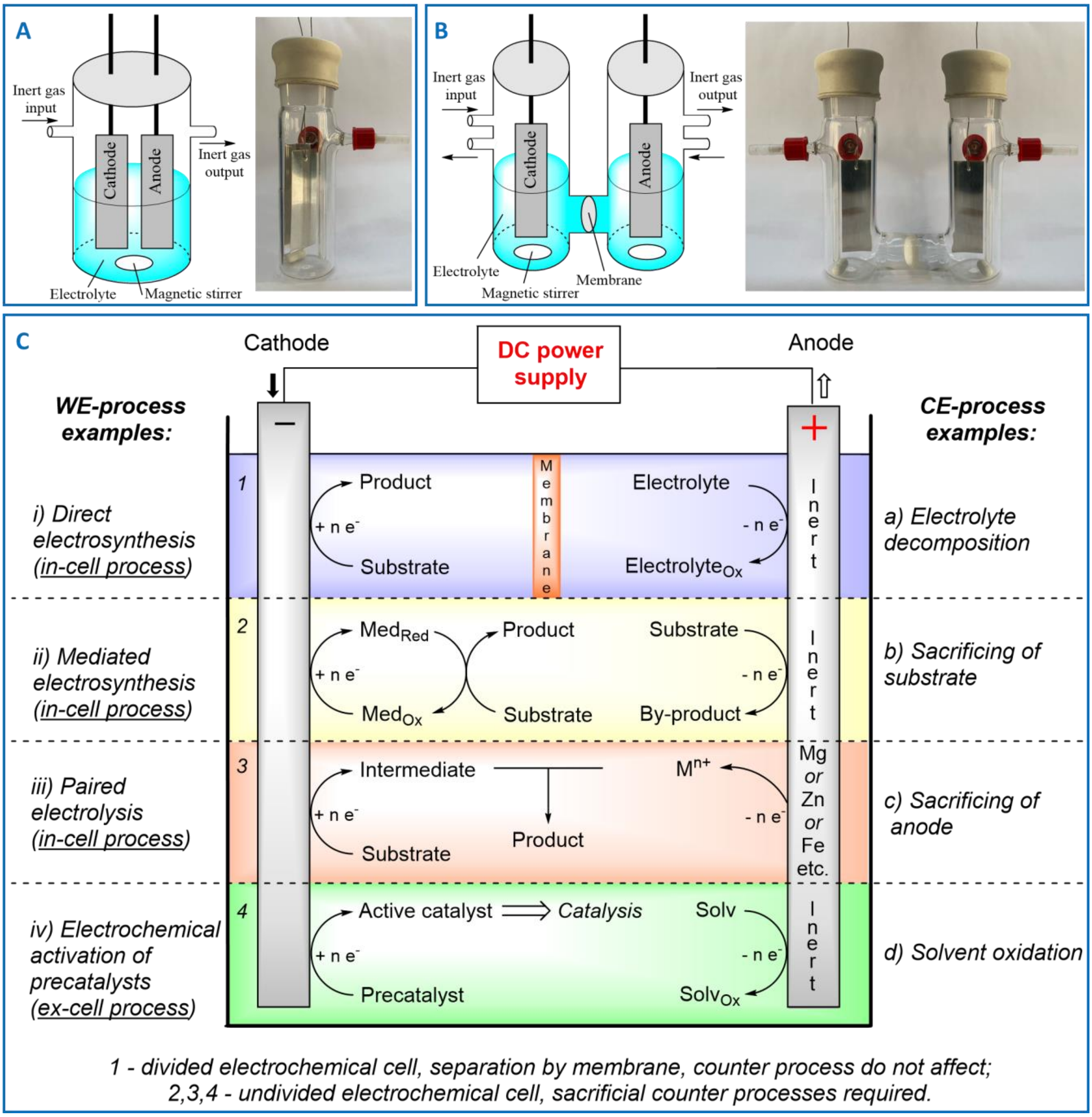


Figure 1. Electrochemical methods applied in synthetic electrochemistry. Design of the electrochemical cells: A) undivided cell, B) divided cell with membrane to separate anolyte and catholyte; and electron transfer processes (C).

The electrochemical methods have been successfully applied for the synthesis of various organic (oxidation of carboxylates, sulfinic acid salts, amines and amides, alcohols as well as reduction of aldehydes and ketones, esters and amides, alkyl halides and many other substrates) [20] and inorganic (chlor-alkali electrolysis and aluminium production) compounds [21]. Though, there are several reviews devoted to the organic and inorganic synthetic electrochemical methods are known in the literature [3,5,13,20–26], the application of the electrochemical techniques for the synthesis of organometallic compounds is presented limitedly. Thus, the aim of this review is to summarize main advances currently developed in synthetic organometallic electrochemistry.

Whereas, organometallics have a wide range of applications, starting from agricultural and biological fields to homogeneous catalysis, where the target products include different types of polymers, pharmaceuticals, and many other practically important compounds [27–42]. The traditional approaches for synthesis of organometallic compounds are usually based on the ecologically unsafe techniques (use of toxic metal chlorides), harsh conditions, employment of expensive reagents and often associated with low-yields and formation of various by-products [43–49]. However, the electrochemical methods are considered as green and sustainable techniques, since they are relying on the use of the most convenient and easily available type of energy and known to be selective and atom-economic [50,51]. Thus, the application of electrochemical synthetic protocols can be regarded as a greener and powerful tool for the preparation of organometallics of different types [34,52–54].

It is worth noting that the number of recent publications regarding the electrochemistry of organometallics according to the Web of Science has increased significantly, with about 40 articles in the last five years (Figure 2).

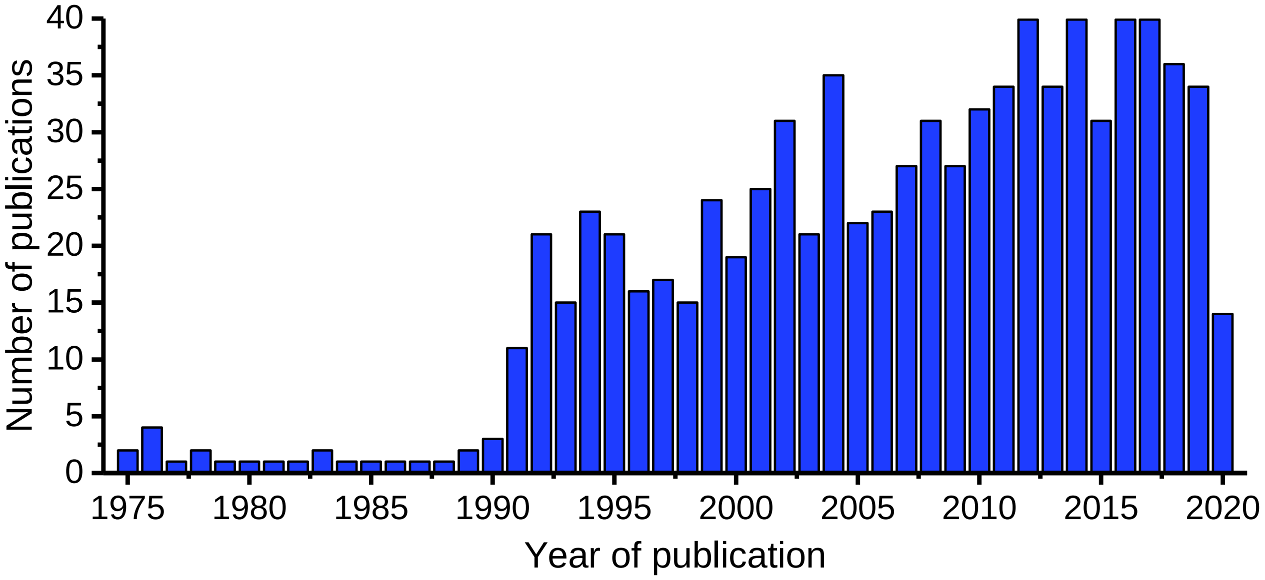


Figure 2. Publications using "electrochemistry" and "organometallics" as keywords from the Web of Science.

Undoubtedly, the organometallic chemistry based on transition metal derivatives has been initiated with investigations of Dessy group in 1966 [55–64]. Now, more than 50 years later, the electrochemistry has been applied in different fields of science, including physical, spectroscopic, synthetic, etc. The excellent systematic review devoted to the evolution of organometallic electrochemistry from its origin with ferrocene was published by William E. Geiger [65], while the theory, techniques, structure and reactions of transition-metal radicals, and the electron-transfer activation, with accent on catalysis were nicely summarized by Didier Astruc [66]. The electrosynthesis of metal complexes (without carbon–metal bond) was also described elsewhere [54,67–77]. Thus, this micro-review discusses the most useful and intriguing modern electrochemical methods for green and convenient generation and (or) *in situ* application of organometallic compounds like direct electrochemical synthesis of organometallics by formation of carbon-metal bond, electrosynthesis of organic compounds mediated by *in situ* generated organometallics, as well as cyclic voltammetry of organometallics and related methods.

2. Direct electrochemical synthesis of organometallics by formation of metal–carbon bond

2.1. A brief overview of the 20th century

To the best of our knowledge, the application of the electrochemical techniques for generation of organometallic species origins in the early 1900-1920s with the pioneering studies of Tafel [78] and Hein [79,80]. Tafel investigated the electrolysis of acidic aqueous solutions of ketones, using mercury cathode, which led to dialkyl-based organometallics (Figure 3a; Table 1, entry 1). Hein studied the sacrificing of metal anodes (Pb or Bi) in the presence of sodium ethyl in diethylzinc and triethylaluminium solutions, which led to the formation of lead and bismuth alkyls. Later, in 1950s Ziegler and Lehmkuhl performed the electrolysis of organic halide solution on aluminium anode with the formation of metal alkyls [77]. Tomilov in 1960’s performed electrolysis of different unsaturated nitriles, leading to carbon-metal bond formation (Figure 3b; Table 1, entry 2) [72]. 1980’s was a period, when electrochemical approach was applied for the synthesis of organometallic halides of main group elements and transition metals (Figure 3c; Table 1, entries 3-7) [81–85]. Some products of these processes were stabilized by adding the neutral donors like 2,2′-bipyridine and 1,10-phenanthroline. The proposed mechanism for these reactions involves the cathodic reduction of an organic halide followed by migration of the halide ion to the anode where MX is formed, further oxidative addition to starting organic halide yields R_nMX_m species. In parallel, in 1980-1990’s the electrosynthesis of metallocenes and their derivatives was performed (Figure 3d; Table 1, entry 8) [76,86]. The electrochemical approach derives metallocenes and its derivatives directly from the metal anode and cyclopentadiene, the latter undergoing one electron reduction on the cathode with evolution of hydrogen. Complexes were isolated as pure products of excellent purity and crystallinity. Analogously, the weak C-H bond of phenylacetylene can be cleaved by electrical means rather than by alkali, with the formation of corresponding phenylacetylides (Table 1, entry 9) [86]. Phenylacetylides of iron, cobalt and nickel should be stabilized by imine ligands due to their high reactivity. It is also worth mentioning the electrochemical preparation of metal carbonyls by the electrolysis of metal precursor (complex or metal plate as anode) under the pressure of carbon monoxide CO [75]. This process produces carbonyls of chromium, vanadium, manganese, iron, cobalt and nickel. The one-pot electrochemical synthesis at room temperature is a cost-effective alternative to classical transmetalation processes.

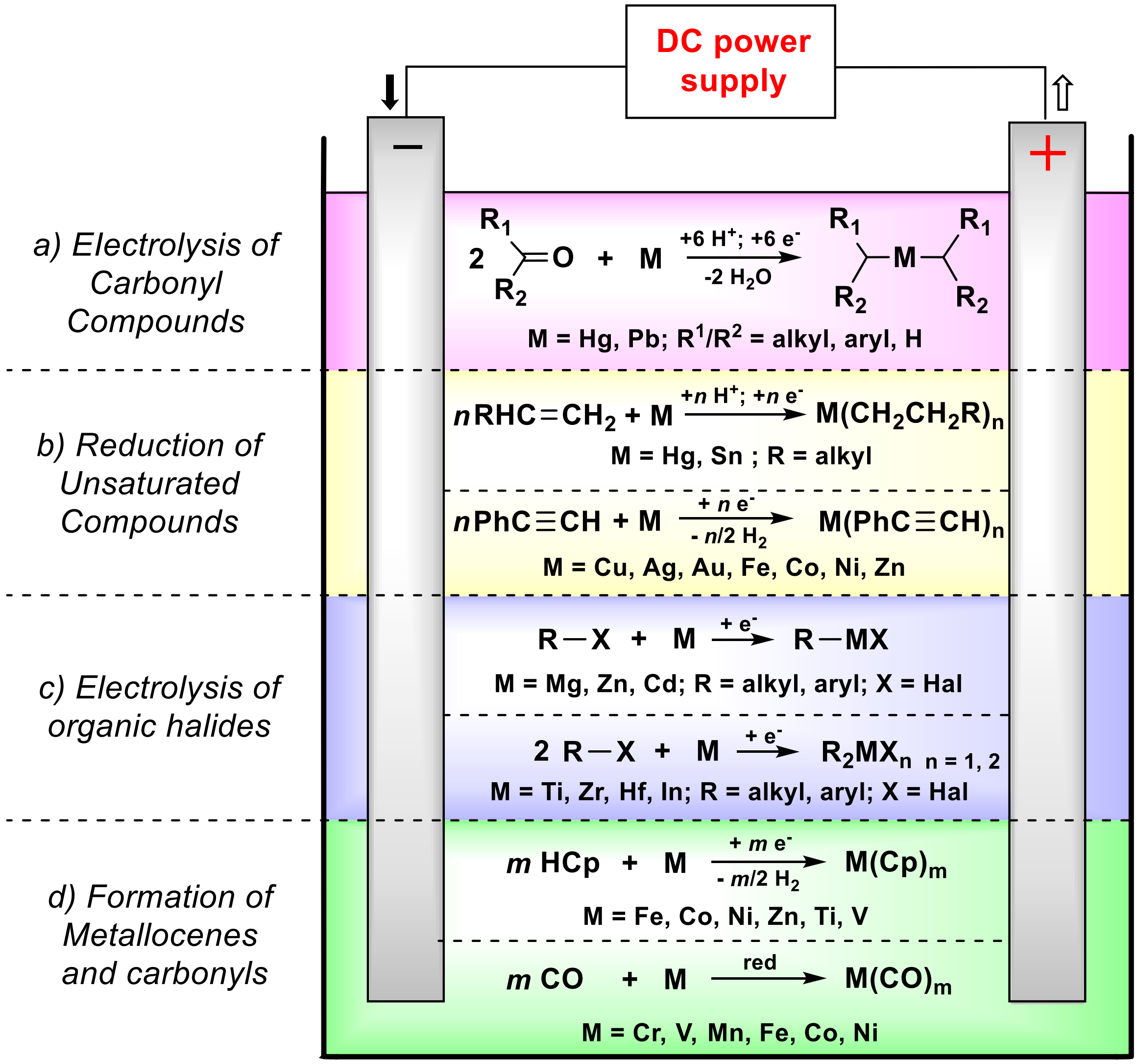
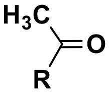
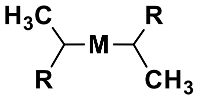
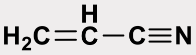
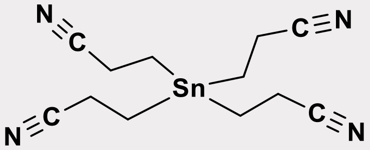
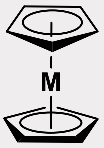
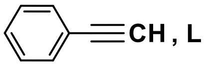
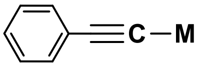


Figure 3. A brief overview of synthetic organometallic electrochemistry of the 20th century.

Table 1. Organometallics generated electrochemically in 20th century.

Entry	Substrate	Product	Ref.
1	 R = Me, Et	 M = Hg, Pb	[72]
2	 $H_2C{=}\overset{H}{C}{-}C{\equiv}N$		[72]
3	RX, bpy R = Me, Et, Ph, Bn, CF_3, C_6F_5, C_3H_3; X = Cl, Br, I bpy = 2,2'-bipyridine	RZnX• bpy or $[RZnX_2]^-$	[81]
4	RC_6H_4X, bpy R = *o*-NC, *o*-NO_2; X = Cl, Br, I bpy = 2,2'-bipyridine	RC_6H_4MX• bpy M = Zn, Cd	[82]
5	RX, L R = Me, Et, Ph, Bn, ; X = Cl, Br, I L = CH_3CN, 2,2'-bipyridine	R_2MX_2•L or R_3MX M = Ti, Zr, Hf	[83]
6	RX, bpy R = Et, Ph, Bn, C_6F_5,; X = Cl, Br, I bpy = 2,2'-bipyridine	R_2InX_2• bpy or R_2InX•bpy	[84]
7	RX, bpy R = Et, ^{n}Bu, Ph, C_3F_7; X = Cl, Br, I bpy = 2,2'-bipyridine	RMgX•bpy or $RMgX_2$•2 bpy	[85]

8	 , CO	 M = Fe, Ni, Co, Zn or $(Cp)_nM(CO)_m$ M = Ti, V, Co, Ni	[86]
9	 L = 2,2'-bipyridine, or 1,10-phenanthroline	 M = Cu, Ag, Au or $M(PhC{\equiv}C)_n \bullet L$ M = Cu, Ag, Au, Fe, Ni, Co, Zn,	[86]

2.2. 21st century advances

Over the past two decades, a big effort has been carried out on the development of new strategies for the synthesis of organometallic compounds. Most of these protocols involves the electrooxidation of metal anodes, which serves as metal precursor, in the presence of the corresponding (pro)ligand. The electrosynthetic processes may be carried out under galvanostatic or potentiostatic conditions, applying direct current (DC) or alternating current (AC), using divided or undivided electrochemical cells, which can be modified according to the Schlenk techniques. The products (organometallics) may contain carbon-metal σ-bonds (cyano-, N-heterocyclic carbene or M—Aryl complexes) or π-bonds (cyclopentadienyl and allyl complexes). In this subchapter the recent advances in synthetic organometallic chemistry are discussed.

2.2.1. Electrochemical synthesis of cyano copper (I) complexes

Kamte and coworkers described the paired electrolysis of an acetonitrile solution of malononitrile in undivided electrochemical cell supplied with sacrificial copper anode and platinum cathode under galvanostatic conditions (constant current density of 4.2 mA × cm^{-2}) [87]. This interaction leads to the formation of cyano copper (I) complexes by the reductive cleavage of the malononitrile molecules at the cathode with the generation of cyanide ion, capable to form the complexes with copper (I) ions, derived from anode (Figure 4). In the presence of 2,2′-bipyridine the complex $[Cu(CN)(bpy)(PPh_3)]$ was obtained (yield: 56.2%) and it's molecular structure was determined by single-crystal X-Ray analysis (Figure 5), which confirms, that the copper ion has distorted tetrahedral geometry. The same method was used for the electrosynthesis of some other Cu(I) complexes with a cyanide ligand $[Cu_2(\mu\text{-}CN)(CH_3CN)_3]CH(CN)_2$, $[Cu_2(\mu\text{-}CN)(PPh_3)_4]CH(CN)_2$ and $[Cu_2(\mu\text{-}CN)(phen)_2(PPh_3)_2]$ [88], the structure of the latter was also confirmed by X-Ray analysis (Figure 5). The IR and ESI-MS spectra of the complexes confirm their polymeric nature.

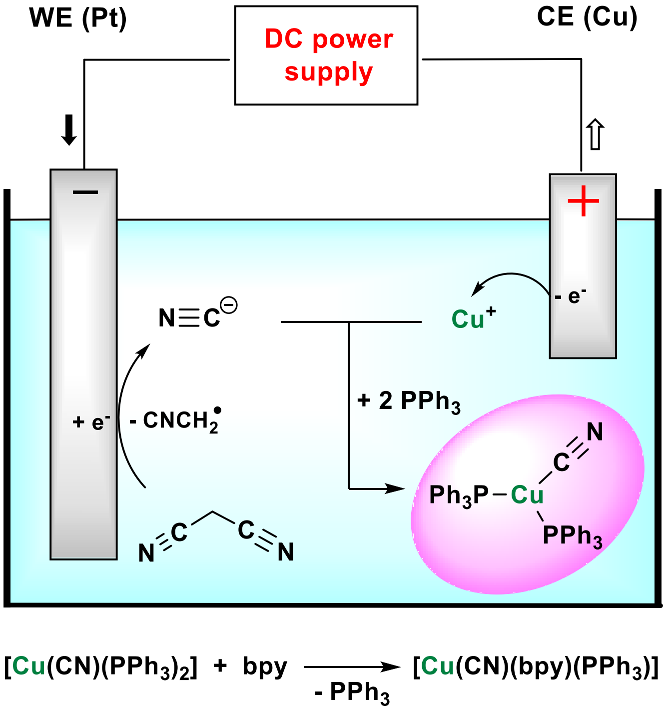


Figure 4. Representation of the electrochemical synthesis of cyano copper (I) complex in acetonitrile in the presence of Bu_4NBF_4 as supporting electrolyte in galvanostatic conditions [87].

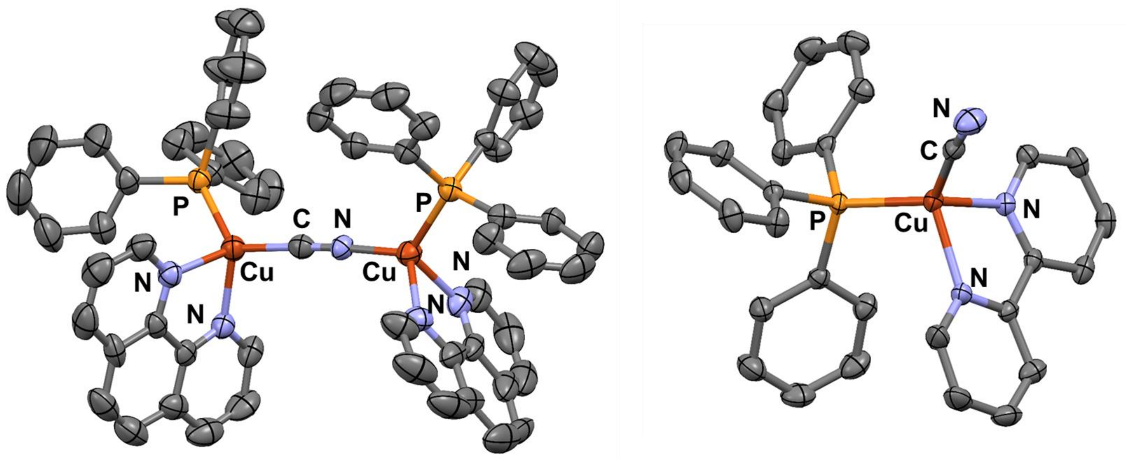


Figure 5. Molecular structures of $[Cu_2(\mu\text{-}CN)(phen)_2(PPh_3)_2]$ (left) [88] and $[Cu(CN)(bpy)(PPh_3)]$ (right) [87].

2.2.2. Electrochemical synthesis of organorhenium cyclopentadienyl complex

Huang *et al*. reported the electrochemical synthesis of organorhenium hydride complex [ReClCp(H)(dppe)] with 68.7% yield, where dppe is bis(diphenylphosphino)ethane, Cp = cyclopentadienyl, in a divided electrochemical cell (in a fritted three-chamber sample holder with separated compartments) under potentiostatic conditions at −1.4 or −1.9 V (Figure 6) [89]. The reduction of the starting complex $[ReCl_3(dppe)(PPh_3)]$ on carbon mesh cathode (WE) in the presence of cyclopentadiene leads to target organometallic *via* an ECE process. The platinum wire was used as the counter electrode with Fc/Fc^+ couple as a sacrificial process, and the silver wire was used as the pseudoreference electrode. Interestingly, when the reaction is performed under nitrogen atmosphere, intermediately formed Re(I) species $[ReCl_2(dppe)(PPh_3)]^-$ ligates N_2 to form $[ReCl_2(N_2)(dppe)(PPh_3)]^-$ by-product, decreasing the yield. Thus, the good yield of 68.7% and the excellent 96.8% Faradaic efficiency was achieved with excess CpH at −1.4 V on a carbon mesh electrode under argon atmosphere. The structure of the organorhenium hydride complex was confirmed by NMR spectroscopy and X-Ray analysis (Figure 7). ^1H NMR spectrum of the half-sandwich rhenium(III) hydride complex [ReClCp(H)(dppe)] exhibits diagnostic upfield resonances characteristic for a transition metal hydride (triplet at −12.22 ppm with $J_{P\text{–}H}$ = 48.8 Hz). The direct electrochemical syntheses of other metallocenes including ferrocene [69] was also reported.

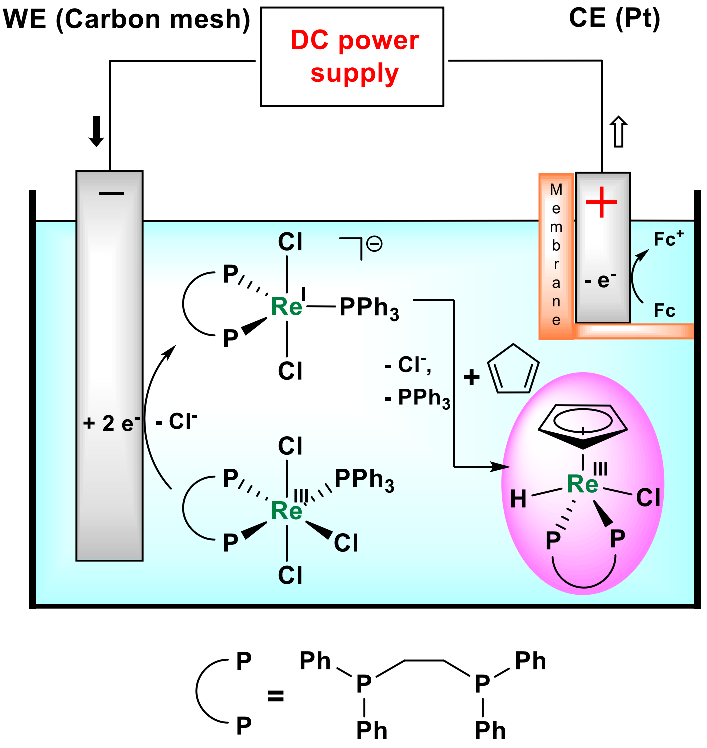


Figure 6. Representation of the electrochemical synthesis of [ReClCp(H)(dppe)] (in $C_6H_4F_2$ with 0.25 M $[Bu_4N][PF_6]$ under potentiostatic conditions at −1.4 or −1.9 V) [89].

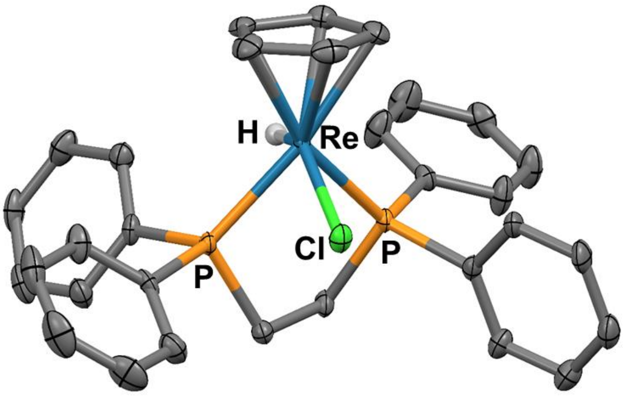


Figure 7. Molecular structure of the electrochemically prepared [ReClCp(H)(dppe)] [89].

2.2.3. Electrochemical synthesis of N-heterocyclic carbene complexes

The electrochemical approach may be applied for the synthesis of *N*-heterocyclic carbene complexes of iron, nickel, copper and gold. Liu and coworkers described the first example of this method [90], using the undivided electrochemical cell at a constant current (50 mA). The imidazolium salts as carbene sources and metal plates as source of metal ion have been used. At the first stage of paired electrolysis, an imidazolium cation undergoes one-electrode reduction on platinum cathode with the formation of *N*-heterocyclic carbene species and hydrogen radicals (Figure 8). Simultaneously, the anodic dissolution of the metal anode occurs. Then, the species formed on the anode and the cathode, combine together to give the corresponding *N*-heterocyclic carbene complexes. Thus, Liu *el al.* reported the electrosynthesis of Cu, Ni and Fe complexes of different composition (Table 2, entries 1-12) [90]. The procedure is simple and avoid the application of expensive and air-sensitive reductants. The synthesis takes place at room temperature and does not require the supporting electrolyte (since imidazolium salts is an excellent conducting material). Molecular hydrogen is only one formed by-product in this process. All obtained complexes have been isolated and X-Ray analysis was performed for 1,3-bis(2-pyridyl)imidazolium-based trinuclear Cu(I) complex, which consists of a triangular Cu_3 core bridged by three NHCs (Table 2, entry 2; Figure 9). This method has been also nicely applied for the preparation of some iron complexes (Table 2, entries 11 and 12; Figure 9). Following this approach, Chapman and coauthors demonstrated the electrosynthesis of a series of Cu(I) mono- and bis-*N*-heterocyclic carbene complexes in an electrochemical flow-cell (Table 2, entries 13-17) [91]. The *in situ* generated complexes have been directly involved in the hydrosilylation reactions of functionalized ketones, where they showed good catalytic activity. Finally, Galuppo and coworkers performed the electrochemical synthesis of gold *N*-heterocyclic carbene complexes with moderate yields using an undivided cell supplied with two gold electrodes under potentiostatic (10 V) conditions [92]. It also should be noted, that an alternative method for electrosynthesis of iron, nickel and copper complexes, using silver *N*-heterocyclic carbene complexes as a carbene sources was reported [90].

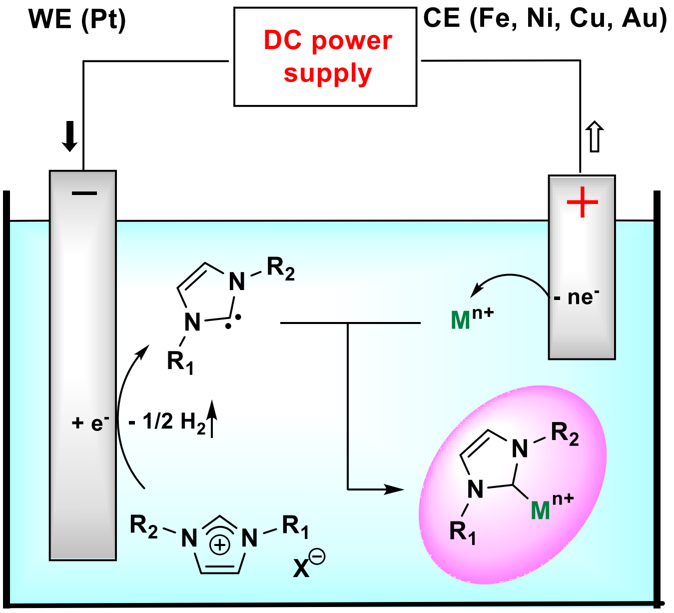
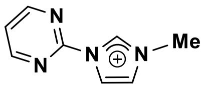
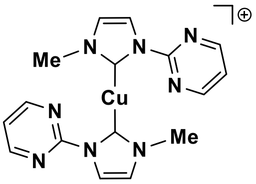
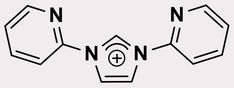
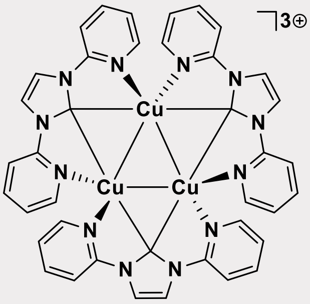
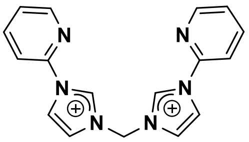
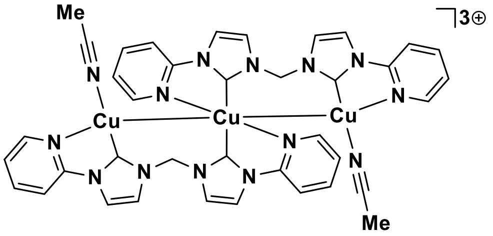
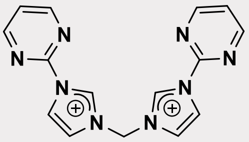
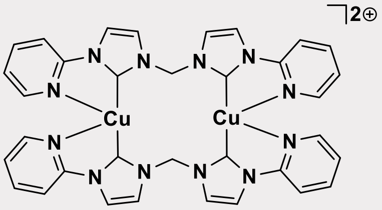
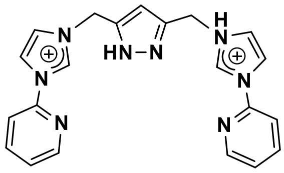
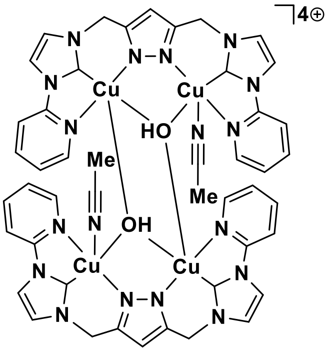
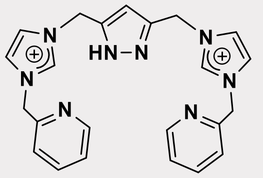
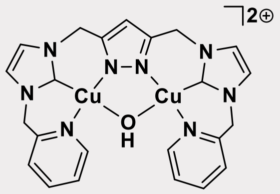
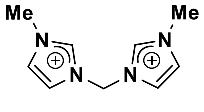
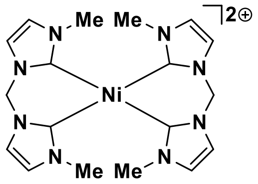
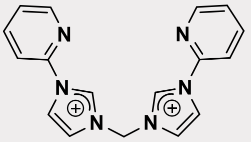
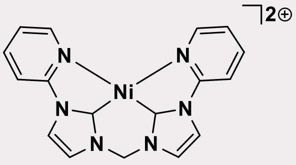
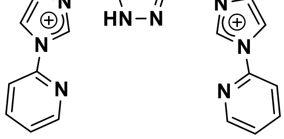
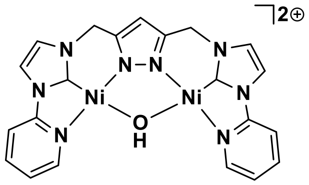
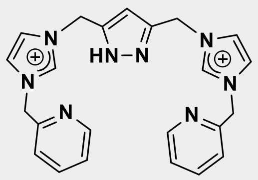
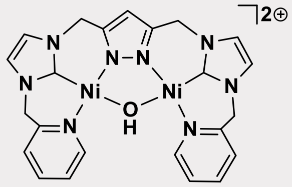
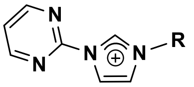
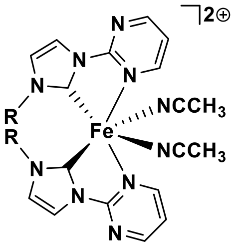
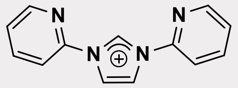
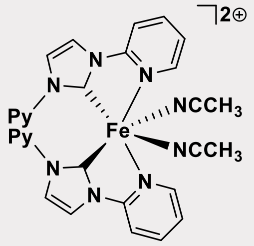
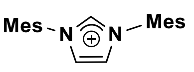
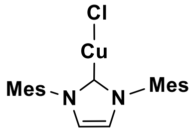
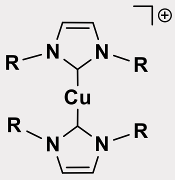
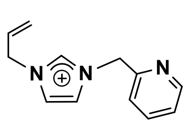
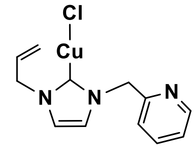
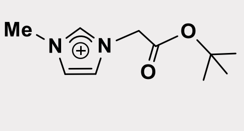
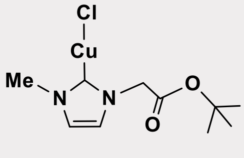


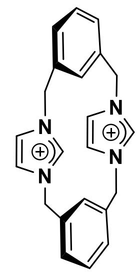
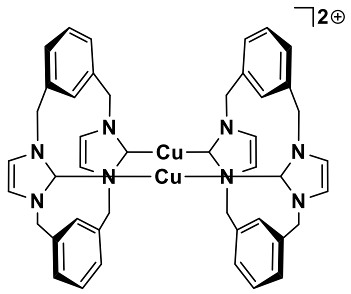
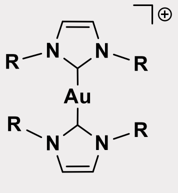
Figure 8. Representation of the electrochemical synthesis of *N*-heterocyclic carbene complexes in acetonitrile [90].

Table 2. Electrochemically synthesized *N*-heterocyclic carbene complexes.

Entry	Imidazolium cation	Product	Yield (%)	Ref.
1			**89**	[90]
2			**78**	[90]

3			**83**	[90]
4			**77**	[90]
5			**60**	[90]
6			**68**	[90]
7			**43**	[90]
8			**54**	[90]
9			**32**	[90]

10			**37**	[90]
11	 R = Me or Ph	 R = Me or Ph	**33** **(R = Me)** **22** **(R = Ph)**	[90]
12			**24**	[90]
13			**93**	[91]
14	 R = Mes, Bn	 R = Mes, Bn	**94** **(R = Mes)** **94** **(R = Bn)**	[91]
15			**91**	[91]
16			**95**	[91]

17			**95**	[91]
18	 R = Mes, Ph	 R = Mes, Ph	**11** **(R = Mes)** **24** **(R = Ph)**	[92]

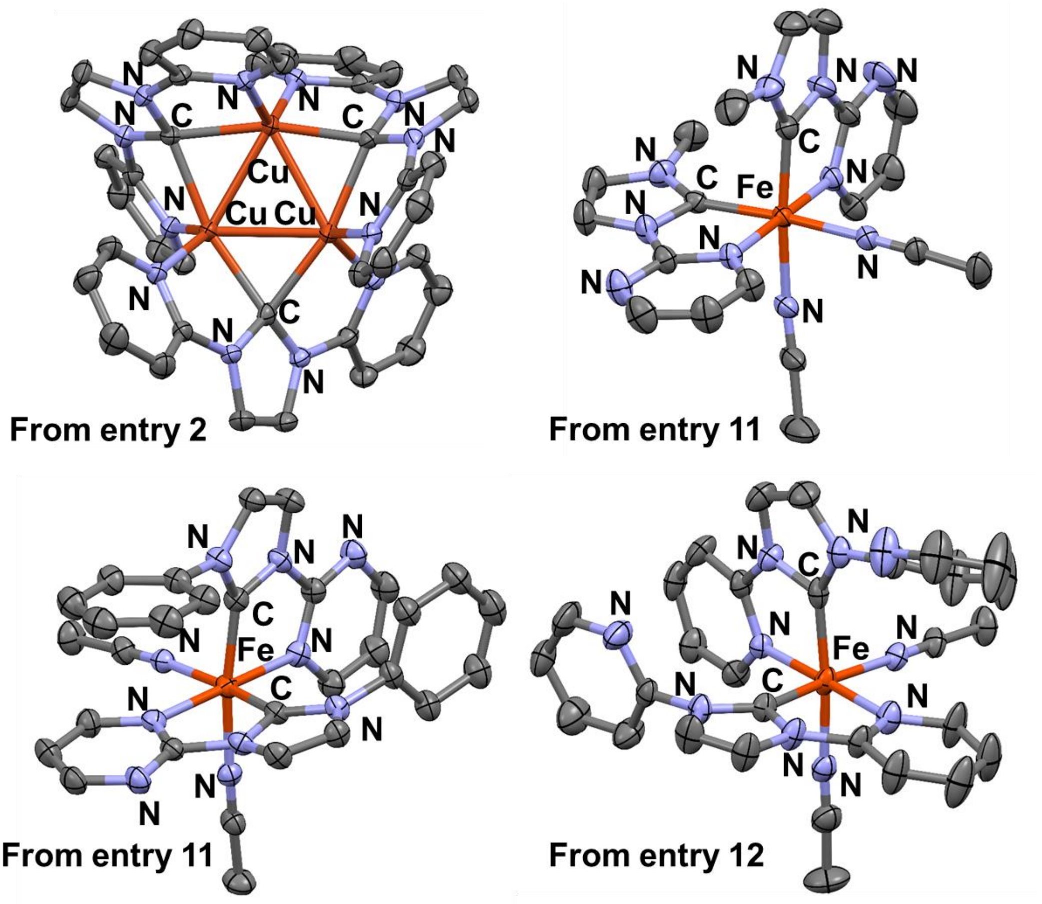


Figure 9. Molecular structures of the electrochemically synthesized *N*-heterocyclic carbene complexes from Table 2 [90].

2.2.4. Electrochemical synthesis of organocopper (I) π-complexes

Hordiychuk and coworkers described the electrochemical synthesis of high-quality single crystals of organocopper π-complexes with allyl-derivatives of various heterocycles using alternating current of 50 Hz applying the voltage of 0.55-0.60 V for 3-4 days to both wire electrodes in an undivided electrochemical cell (Figure 10) [93,94]. The starting material for this electrolysis is acetonitrile solution of corresponding ligand and copper(II) halide. Cu(I), which has been formed by reduction of Cu(II) ion on the electrode, ligates the corresponding allyl-derivative with the formation of final π-complex. This method allowed to obtain a series of organocopper complexes or heterobimetallic Cu^{I}–Ag^{I}, Cu^{I}–Zn^{II}, Cu^{I}–Fe^{II} species using the corresponding metal electrode as well as mixed-valence Cu^{I}– Cu^{II} complexes with an 1,2,4-triazole allyl-derivative. Crystals of these compounds appeared directly on the electrode surface. Fedorchuk *et al.* also worked in this direction and demonstrated the electrosynthesis of a series of Cu(I) π-coordination compounds with (2Z)-2-(phenylimino)-3-allyl-1,3-thiazolidin-4-one (papt) and (2Z)-2-[(2-hydroxyethyl)imino]-3-allyl-1,3- thiazolidin-4-one (eapt) ligands [95,96]. Some of the generated complexes were characterized by X-Ray analysis (Figure 11). In complex $[Cu(papt)NO_3]$ the organic ligand is a chelate, responsible for the formation of a seven-membered cycle. Similarly, in the binuclear complexes $[Cu_2(papt)_2Hal_2]$, where Hal is Cl or Br, ligand papt is π-chelate attached to the metal through the N-atom and the C=C bond of the allyl group forming the seven-membered $\{C_4N_2Cu\}$ metallocycles. In the structure of $[Cu_2(L)_2Ag_2Cl_4]$ {L = (3-allylsulfanyl-4-allyl-5-phenyl-4H-1,2,4-triazole} inorganic part is represented by flat and symmetric $[Ag_2Cl_4]$ unit, while structures of complexes $[Cu_2(L)_2MCl_4]$ based on a different construction mode – the inorganic part is represented by a $[MCl_4]^{2-}$ anion, where M is Zn(II) or Fe(II). This anion binds two copper(I) ions of the $\{Cu_2(L)_2\}^{2+}$ core in a bridging manner. The Cu-C_m (C_m is a middle point of C═C bond) distance in these complexes is in the range of 1.914(3)–1.964(2) Å. Such organocopper (I) π-complexes becoming attractive objects for modern interdisciplinary research due to their catalytic, anticancer, photoluminescent, ferroelectric and nonlinear optical properties.

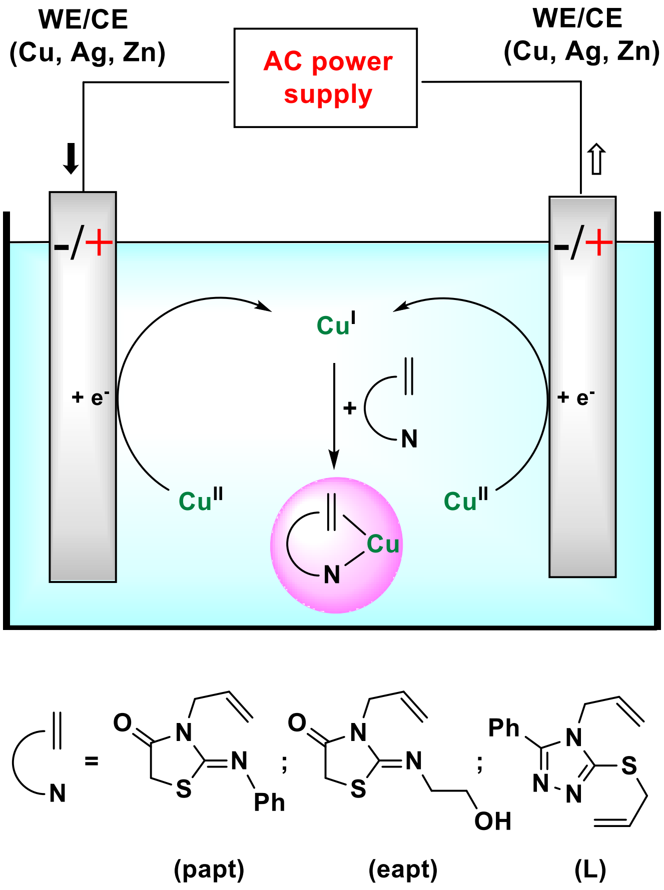


Figure 10. Representation of the electrochemical synthesis of organocopper π-complexes in acetonitrile applying alternating current of 50 Hz [93,94].

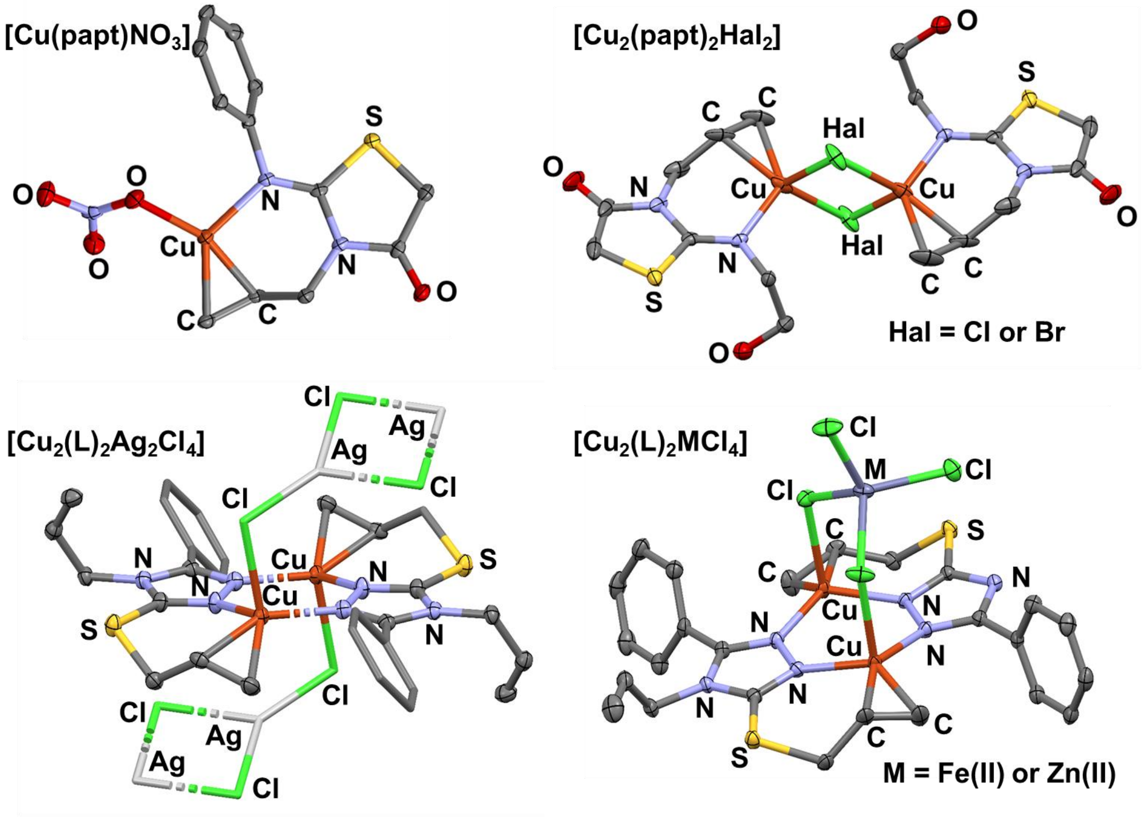


Figure 11. Molecular structures of some electrochemically synthesized organocopper (I) π-complexes {L = (3-allylsulfanyl-4-allyl-5-phenyl-4H-1,2,4-triazole} [93–96].

2.2.5. Electrochemical synthesis of organonickel σ-complexes [NiBr(Aryl)(bpy)]

Some of us reported straightforward one-pot electrosynthesis of nickel complexes bearing metal-carbon sigma-bond [97–100]. This method operates under mild conditions using divided or undivided electrochemical cell, equipped with platinum or nickel cathode (working electrode) and sacrificial metal anode out of magnesium, zinc, aluminum or nickel (counter electrode). The oxidation potential of counter electrode process (dissolution of the corresponding metal anode with the formation of related metal ions Mg^{2+}, Zn^{2+}, Al^{3+} or Ni^{2+}) allows the working electrode process to proceed [99,101]. On the first stage of the electrolysis the starting nickel complex [$Ni^{II}Br_2$(bpy)] (bpy is 2,2′-bipyridine) undergo two-electron reduction on the WE with generation of nickel (0) species [Ni^0(bpy)], followed by their oxidative addition to *ortho*-substituted aromatic bromides with the formation of target organonickel complex [Ni^{II}Br(Aryl)(bpy)] (Figure 12).

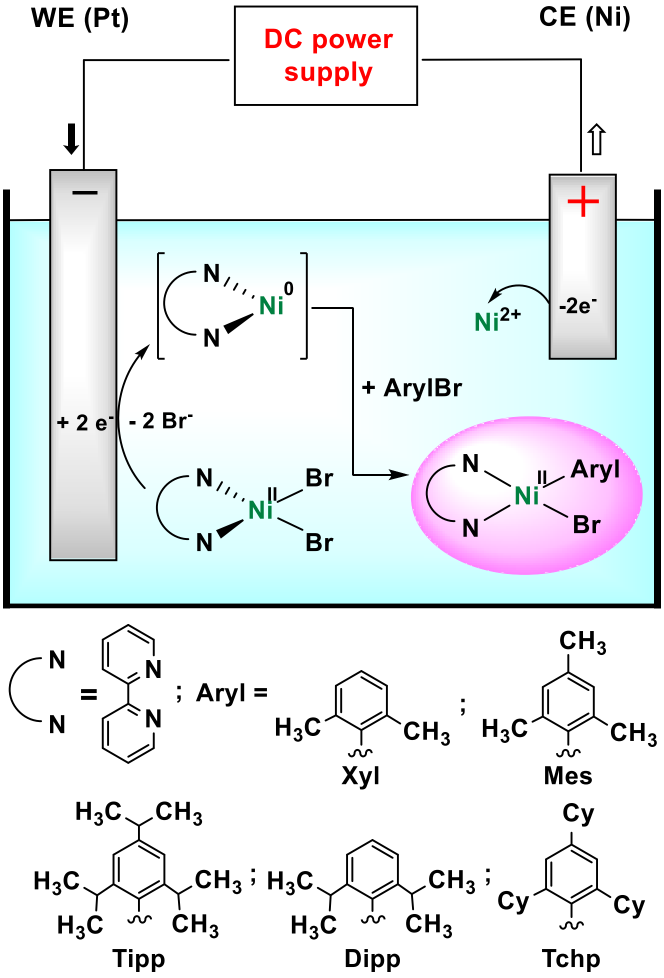
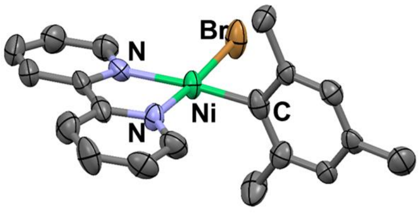


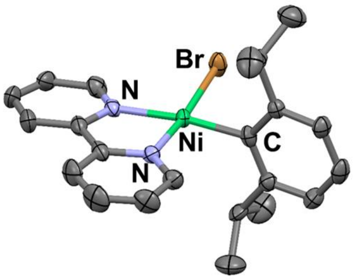
Figure 12. Representation of the electrochemical synthesis of organonickel σ-complexes [NiBr(Aryl)(bpy)] in DMF using undivided electrochemical cell [97].

It should be noted, that generation of organonickel complexes with Ni-C(sp^3) or Ni-C(sp^2) bonds without *ortho*-substituents in the aromatic fragment is also possible, however, such species are found to be unstable since the corresponding M-C bond is very unstable. While complexes [NiBr(Aryl)(bpy)], where Aryl is 2,6-dimethylphenyl (Xyl), 2,4,6-trimethylphenyl (Mes), 2,6-diisopropylphenyl (Dipp), 2,4,6-triisopropylphenyl (Tipp), 2,4,6-tricyclohexylphenyl (Tchp), were successfully synthesized using this method, isolated and characterized by X-Ray analysis (Figure 13). However, the Faradaic efficiency is low (~50%) when the undivided electrochemical cell was applied. This is due to competitive process on the working electrode: the reduction of metal ions formed on the anode. Thus, the application of membrane to separate WE and CE compartments allowed us to increase the current yield of organonickel sigma-bonded complexes up to 95%. The progress of the electrolysis can be easily controlled by color change of the reaction mixture. Thus, the starting solution of metal precursor [$Ni^{II}Br_2$(bpy)] is green (high-spin nickel (II) complex), and changes to black when 1F is passed through the electrolyte (the formation of Ni(0) species). Finally, the solution containing formed product [NiBr(Aryl)(bpy)] is red (low-spin nickel (II) complex).

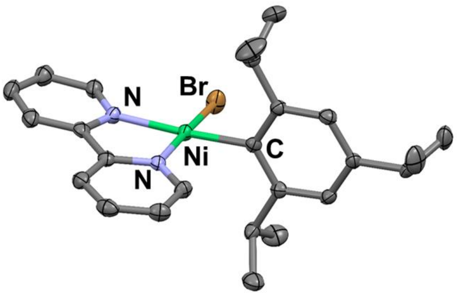
The electrosynthesized organonickel complexes are widely applied for C-C, P-C and N-C bond formation reactions. Thus, [NiBr(Mes)(bpy)] is capable reacting with primary phosphines ($PhPH_2$, $MesPH_2$, *i*-$BuPH_2$, $CyPH_2$) or even with PH_3 leading to secondary phosphines by formation of new C-P bond involving mesityl fragment [102–104]. Complexes [NiBr(Xyl)(bpy)], [NiBr(Mes)(bpy)], [NiBr(Tipp)(bpy)], [NiBr(Tchp)(bpy)] interact with a series of nitriles (acetonitrile, propionitrile, chloroacetonitrile, benzonitrile) leading to imines by the formation of new C-C bond between aromatic fragment and nitrile group C≡N [105].



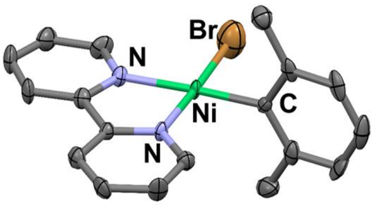
[NiBr(Mes)(bpy)]



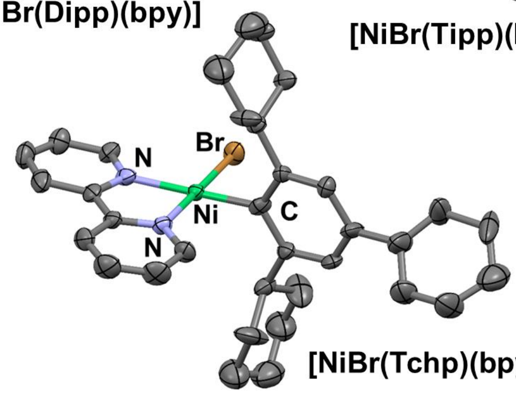
[NiBr(Dipp)(bpy)]



[NiBr(Tipp)(bpy)]



[NiBr(Xyl)(bpy)]



[NiBr(Tchp)(bpy)]

Figure 13. Molecular structures of the electrochemically synthesized organonickel σ-complexes [97,100].

3. Electrosynthesis of organic compounds mediated by *in situ* generated organometallics

It is well known, that organometallic compounds are highly reactive species, therefore, their isolation is not always possible. However, application of such intermediates *in situ* allowed elaborating electrocatalytic methods for C-C bond formation reactions, involving a wide range of substrates [25,106,107]. The most useful and intriguing advances in the electrochemical *in situ* formation of various organometallics for their application in the synthesis of organic compounds are discussed in this chapter.

3.1. Organonickel-mediated electrochemical cross-coupling reactions

The electrochemical allylation, alkylation or arylation of various organics mostly presented by *in situ* generated organonickel reagents [106]. These approaches allows to proceed cross- and homocoupling reactions of organic halides [108–114], carbonylation and carboxylation reactions [115], reductive coupling of organic halides with carbonyl derivatives [116], interaction of organic halides with unsaturated compounds (alkynes and alkenes) [117–121], electroreductive cyclization processes [122], homo-coupling of unsaturated hydrocarbons [123], carboxylation and carbonylation of unsaturated hydrocarbons [124] and some other reactions [115,125,126] (Figure 14). The high-reactive organonickel species are key intermediates of these electrocatalytic processes.

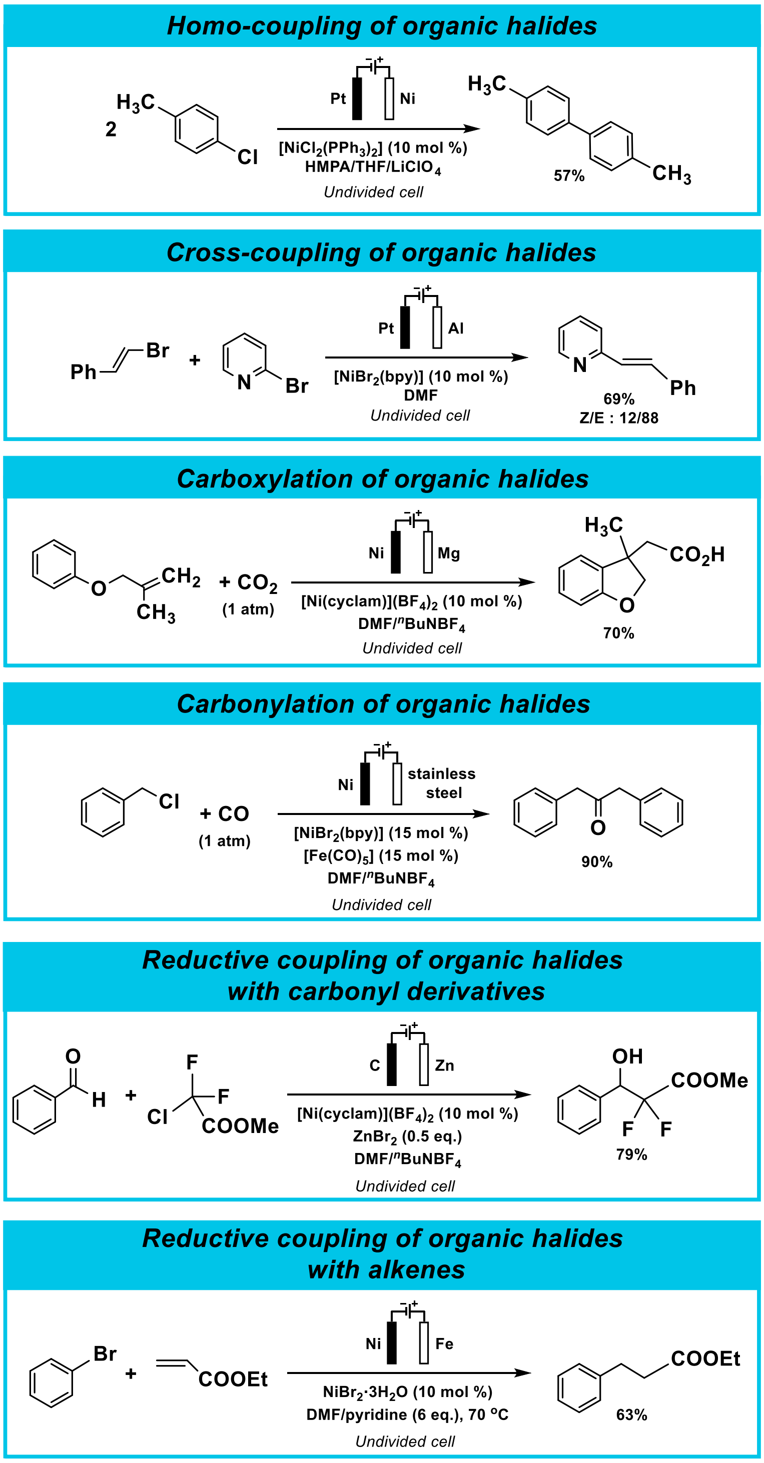


Figure 14. Examples of organonickel-catalyzed electrochemical coupling reactions. Adapted from ref. [115].

Thus, Sengmany and coworker reported an efficient one-pot approach for the synthesis of aryl- and heteroarylpyridazines *via* [NiBr$_2$(bpy)] catalyzed electrochemical cross-coupling reaction of 3-chloro-6-methoxypyridazine and 3-chloro-6-methylpyridazine with a wide range of aryl and heteroaryl halides [127]. It was found, that the reaction proceeds smoothly with the electron withdrawing group-substituted phenyl bromides, while in the absence of the substituent in the phenyl ring, iodine is required as halide. Later, authors expand this method for the synthesis of 3-amino-6-aryl- and 3-amino-6-heteroarylpyridazines [128]. In this case, 3-amino-6-chloropyridazines were used as a starting cross-coupling partner, iron/nickel rod and foam nickel were applied as an anode and a cathode, respectively, in an undivided cell. The process was performed in galvanostatic mode (0.2 A). The authors studied the electrochemical properties of the catalyst [$NiBr_2$(bpy)] in the presence and in the absence of substituted pyridazine using cyclic voltammetry method. Interestingly, they observed two reversible reduction peaks ascribed to $Ni^{II} \rightarrow Ni^{I} \rightarrow Ni^{0}$ conversion in the absence of the substrate, while reversibility of the redox system disappears by an addition of the substituted pyridazine, indicating the formation of organonickel species. Sengmany *et al.* proposed the mechanism of this cross-coupling reaction, initiated by the two-electron reduction of the catalyst with formation of Ni(0) complexes, which then subjected to an oxidative addition onto 4-(6-chloropyridazin-3-yl)morpholine (MPzCl) forming organonickel intermediate (Figure 15). Following one-electron reduction produces corresponding Ni(I) halogen-free species, then, second oxidative addition to aryl halide give Ni(III) complex with two organic groups. Finally, reductive elimination reaction led to desired coupling product by releasing of Ni(I)X species, which are electrochemically reduced to regenerate Ni(0).

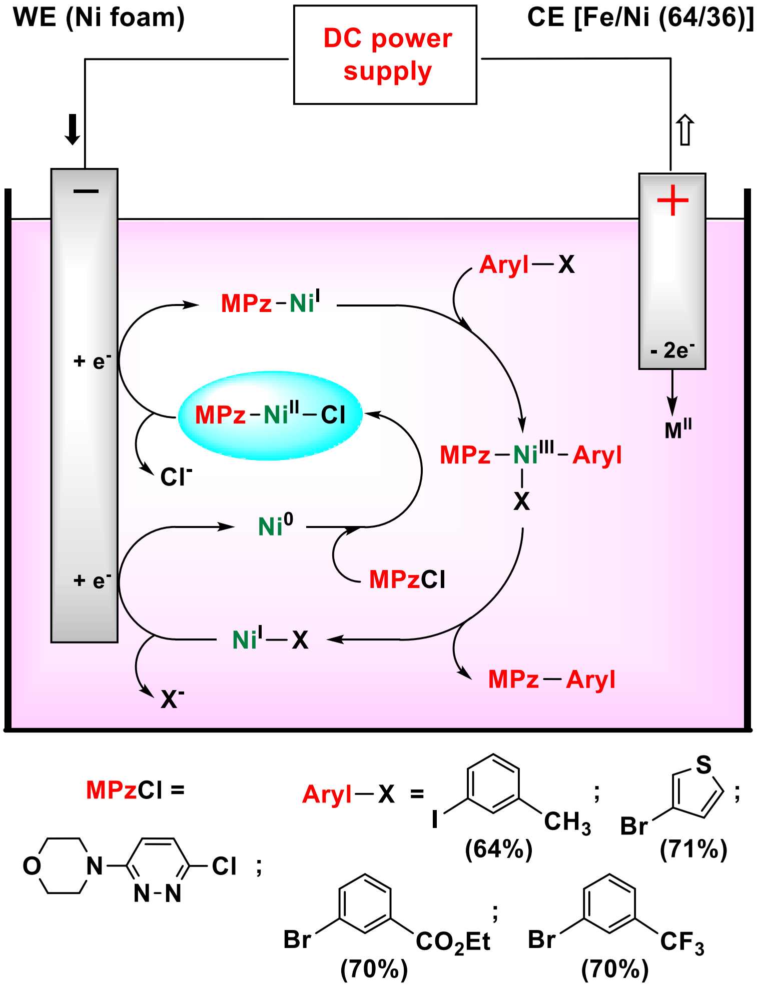


Figure 15. Organonickel-catalyzed electrochemical cross-coupling of 3-amino-6-chloropyridazines and aryl or heteroaryl halides and representative examples [129].

However, Perkins and coauthors reported different catalytic cycle for similar system [129]. They performed C(sp^2)-C(sp^3) cross-coupling reactions between aryl and alkyl bromides using [$NiCl_2$(dme)]/dmbpy catalytic system, where dme is dimethoxyethane, dmbpy is 4,4′-dimethoxy-2,2′-bipyridine, in an undivided electrochemical cell applying sacrificial metal anode (Mg, Zn or Fe) and RVC (reticulated vitreous carbon) cathode under galvanostatic (10-50 mA) conditions. The mechanism proposed by the authors includes a cathodic reduction of nickel complex followed by oxidative addition to the corresponding aryl bromide (Aryl-Br), leading to the formation of organonickel(II) intermediate (Figure 16), which was converted to nickel(III) complex by addition of alkyl halide (R-Br). Consistently, the reductive elimination step produces the desired Aryl-R product and leave Ni(I) species, which additionally are reduced on the working electrode to regenerate the catalyst. The oxidation of metal anode allows the process to be performed in an undivided electrochemical cell. Moreover, authors found, that increasing the temperature to 65 °C enhance the rate of the catalytic cycle.

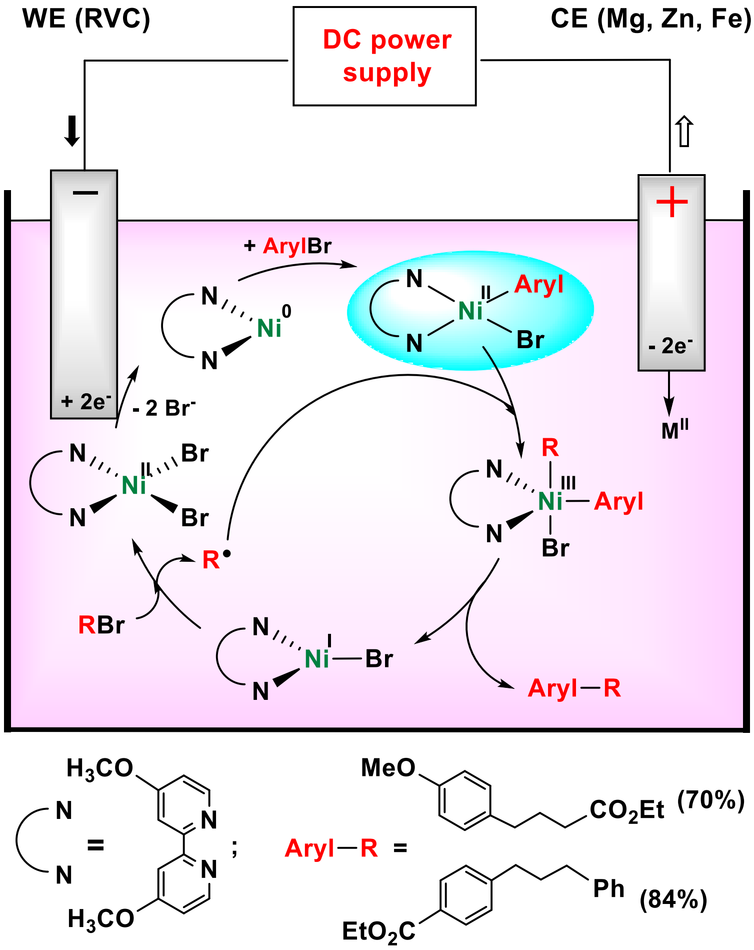


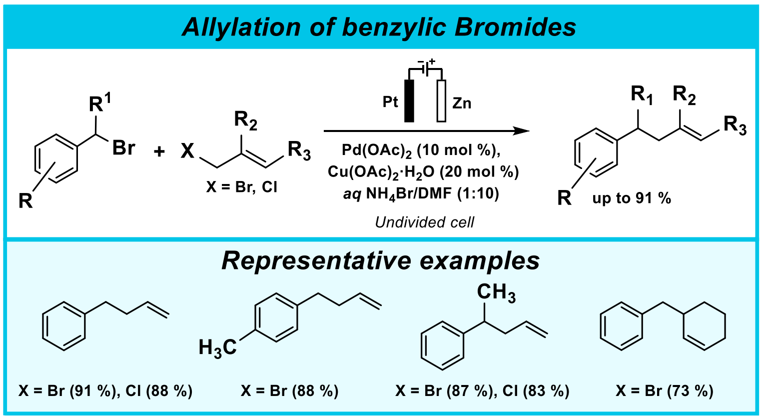
Figure 16. Organonickel-catalyzed electrochemical cross-coupling of organic halides and representative examples (RVC is reticulated vitreous carbon) [129].

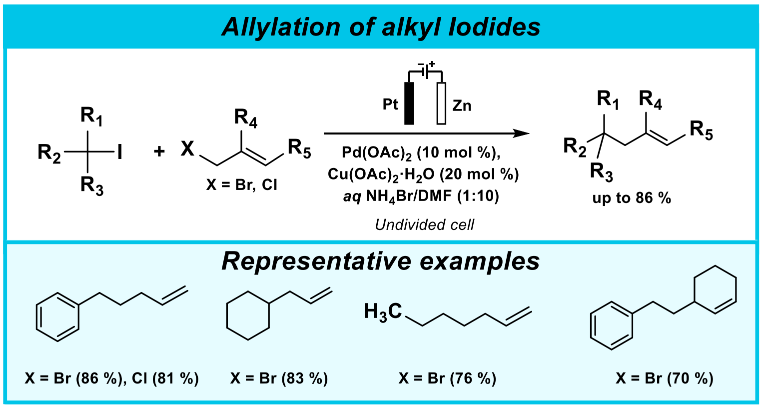
It is nteresting to note, that Li *et al.* performed the electrochemical nickel-catalyzed reductive coupling of *N*-hydroxyphthalimide (NHP) esters with aryl halides in continuous-flow electrochemical cell, which is an example of robust and scalable process [130]. The process operates in divided electrochemical flow cell (nafion membrane) with RVC as the anode and the graphite plate as the cathode under galvanostatic (j = 13.7-38.1 mA × cm^{-3}) conditions, using [$NiBr_2$(dme)]/dtbbpy system (30 mol%, dtbbpy is 4,4′-di-tert-butyl-2,2′-bipyridine). This approach allows obtaining various coupled products by the formation of new $C(sp^2)$-$C(sp^3)$ carbon-carbon bond. According to the author’s mechanistic hypothesis, the reduction of starting NHP on the working electrode (cathode) results in the formation of $C(sp^3)$ radical, while simultaneous cathodic reduction of nickel catalyst in the presence of aryl halide led to generation of organonickel species (as discussed earlier). Interaction of these two reduction products *via* oxidative addition and reductive elimination steps give the final cross-coupling product. The counter electrode process represented by oxidation of the initially added trimethylamine. The common experiment setup includes the *DC power supply*, *syringe pumps*, used to pump the anodic and the cathodic solutions in the *continuous-flow electrochemical reactor*, and *the sample collection vials*.

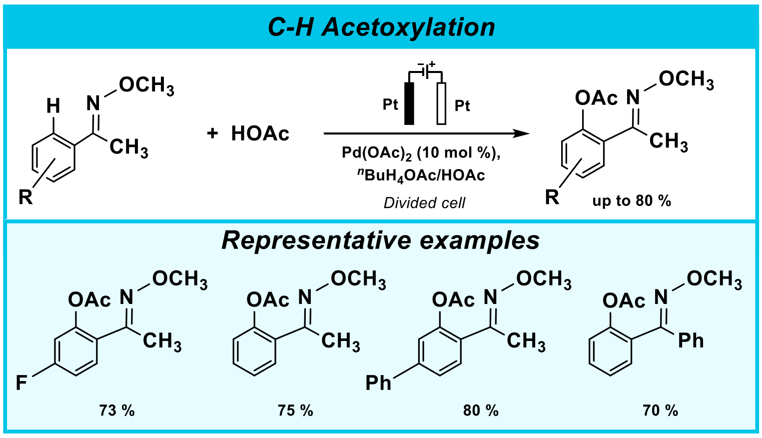
3.2. Organopalladium-mediated electrochemical cross-coupling reactions

Similarly to nickel-based systems, palladium catalysts have been widely applied in different electrochemical C—X bond formation reactions, including $C(sp^2)$—$C(sp^2)$, $C(sp^2)$—$C(sp^3)$, and $C(sp^3)$—$C(sp^3)$ or P—C, N—C and C—halogen bonds [131–142]. As an example, Huang and Lai developed the palladium-catalyzed zinc-mediated electrochemical allylic alkylation in the reaction of alkyl halides with allylic halides in aqueous solution (representative example is shown in Figure 17) [143]. In this approach, authors tested various palladium catalysts and electrode materials. It was found, that $Pd(OAc)_2/Cu(OAc)\cdot H_2O$ system in combination with platinum cathode and zinc anode demonstrates the best efficiency in these processes. Based on the mechanistic investigations the Barbier–Negishi-type coupling reaction was proposed to proceed with the generation of alkylzinc reagents and π-allylic palladium complexes, further transmetalation reaction leads to the final coupling product.

$Pd(OAc)_2$ catalyst was also used for electrochemical $C(sp^2)$—H and $C(sp^3)$—H bond acetoxylation [144,145]. The proposed method allows coupling of various oxygen-containing anions, including acetate, tosylate, and alkoxides with alkanes and arenes. Authors assumed, that after $C(sp^3)$—H or $C(sp^2)$—H bond cleavage, anodic oxidation of the resulting organopalladium(II) intermediate to a high-valent palladium(III) or palladium(IV) species in the presence of oxygen promotes a ligand exchange reaction followed by C—O reductive elimination step forming the corresponding oxygenated product (Figure 17). The same catalyst was applied for electrochemical $C(sp^2)$—H alkylation of arenes [140]. In this approach, alkylboron reagents were coupled with nitrogen-containing aryl substrates in an undivided electrochemical cell. According to mechanistic investigations intermediately generated organopalladium complex could be oxidized on the anode in the presence of potassium trifluoroalkylborate to generate palladium(III) or palladium(IV) species, which could afford methylated product and regenerate palladium(II) species upon the reductive elimination.


Allylation of benzylic Bromides
R^1
Br
R
+
X
R_2
R_3
X = Br, Cl
Pt
Zn
$Pd(OAc)_2$ (10 mol %),
$Cu(OAc)_2 \cdot H_2O$ (20 mol %)
aq NH_4Br/DMF (1:10)
Undivided cell
R_1
R_2
R_3
R
up to 91 %
Representative examples
H_3C
CH_3
X = Br (91 %), Cl (88 %)
X = Br (88 %)
X = Br (87 %), Cl (83 %)
X = Br (73 %)


Allylation of alkyl Iodides
R_1
R_2
I
R_3
+
X
R_4
R_5
X = Br, Cl
Pt
Zn
$Pd(OAc)_2$ (10 mol %),
$Cu(OAc)_2 \cdot H_2O$ (20 mol %)
aq NH_4Br/DMF (1:10)
Undivided cell
R_1
R_4
R_5
R_2
R_3
up to 86 %
Representative examples
H_3C
X = Br (86 %), Cl (81 %)
X = Br (83 %)
X = Br (76 %)
X = Br (70 %)


C-H Acetoxylation
H
N
OCH_3
CH_3
R
+ HOAc
Pt
Pt
$Pd(OAc)_2$ (10 mol %),
$^nBuH_4OAc$/HOAc
Divided cell
OAc
N
OCH_3
CH_3
R
up to 80 %
Representative examples
OAc N OCH_3 CH_3
F
73 %
OAc N OCH_3 CH_3
75 %
OAc N OCH_3 CH_3
Ph
80 %
OAc N OCH_3
Ph
70 %

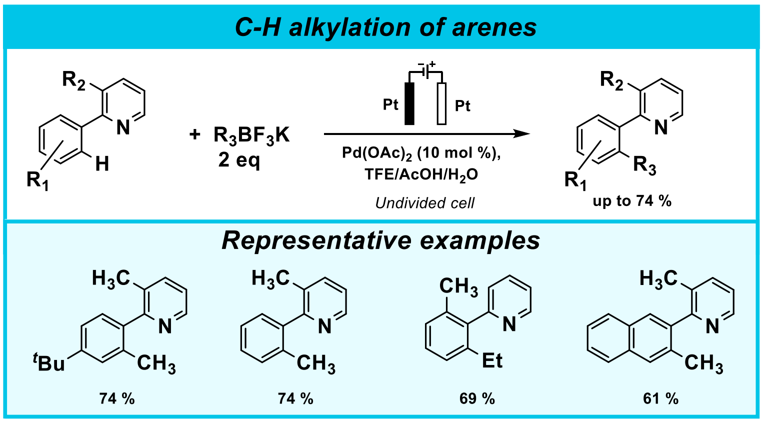

C-H alkylation of arenes
R_2
N
H
R_1
+ R_3BF_3K
2 eq
Pt
Pt
$Pd(OAc)_2$ (10 mol %),
TFE/AcOH/H_2O
Undivided cell
R_2
N
R_3
R_1
up to 74 %
Representative examples
H_3C N ^tBu CH_3
74 %
H_3C N CH_3
74 %
CH_3 N Et
69 %
H_3C N CH_3
61 %

Figure 17. Representative examples of organopalladium-catalyzed electrochemical coupling reactions [140,143,145].

3.3. Organotin-mediated electrochemical synthesis of alcohols

One of the most used metals in electrochemical synthesis of organic compounds is tin, due to its diverse oxidation states (0, 2+, 4+) and relativity low reduction potentials (standard potential E° for $Sn^{2+} \rightarrow Sn^0$ is -0.14 V) [106]. The first example of the application of Sn for allylation of carbonyl compounds with the formation of the corresponding alcohols in methanol media was reported by Uneyama and coworkers [146]. According to the proposed mechanism, Sn powder, used in catalytic amount (10 mol. %), undergoes the oxidative addition to allyl bromide with the intermediate formation of organotin reagent, which further reduces ketones to corresponding allylation products. Subsequently, the reduction of the formed Sn(II) species on the cathode regenerates Sn(0) catalyst. The anodic reaction was formulated as an oxidation of bromide anions. The reaction proceeds at room temperature in an undivided electrochemical cell using platinum foil electrodes under galvanostatic (50 mA) conditions and leads to alcohol derivatives in up to 91% isolated yield. Zhang *et al*. modified this procedure by using of tin(II) chloride as precatalyst, which undergo cathodic reduction to form tin(0) species while the following stages remain the same (Figure 18) [147]. The sustainability of this process is the ultimate feature of this approach. This method was expanded to the synthesis of tertiary alcohols [148]. In this approach, Zhang and coauthors performed the electrolysis of alcohols instead of carbonyl compounds in the presence of $SnCl_2/KNO_3$ mixture in an undivided electrochemical cell. The oxidation of starting secondary alcohols on graphite anode led to formation of aldehydes, while platinum cathode is responsible for the regeneration of Sn(II)/Sn(0) mediator system.

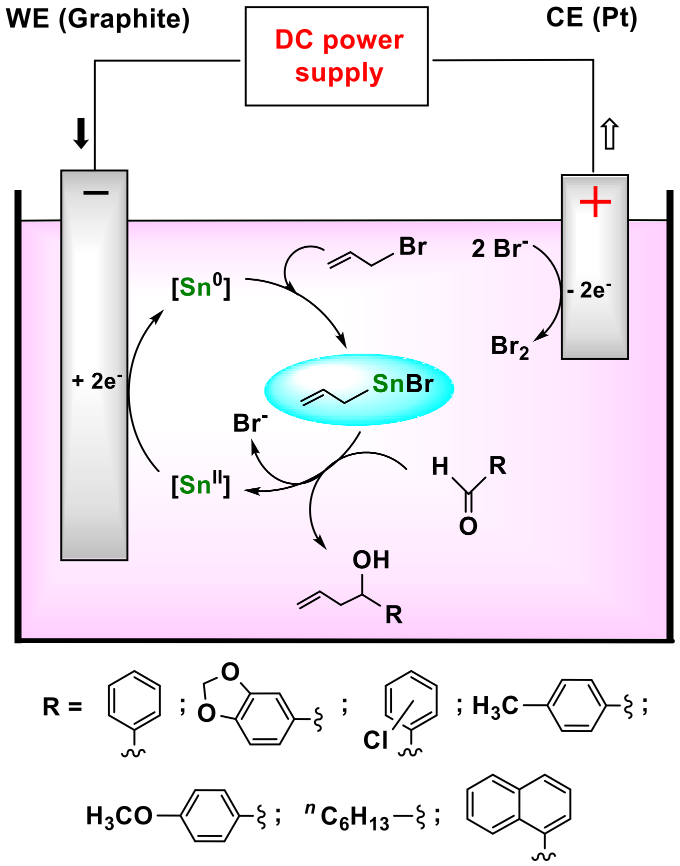


Figure 18. Organotin-mediated electrochemical synthesis of alcohols [147].

3.4. Orgasamarium-mediated electrochemical coupling reactions

Mellah and coworkers demonstrated the electrochemical synthesis of various organics (vicinal diol compound, azobenzenes, homoallylic alcohols and phenylacetic acids) by the electrogenerated samarium salts [149–151]. They have discovered a novel and reliable catalytic system based on the use of a sacrificial samarium electrode as a source of SmI_2. Some representative examples are shown in Figure 19. At the first stage of the electrocatalytic allylation of carbonyl compounds, the constant current of 50 mA passed through the solution of $^{n}Bu_4NPF_6$ in THF in an undivided electrochemical cell, supplied with glassy carbon cathode and samarium anode, for 36 min to produce the catalytic amount of SmI_2. After the pre-electrolysis, starting materials were added, and the polarity of the electrodes were reversed, thus, samarium was served as the cathode. During the second step of the electrochemical process (constant current of 50 mA for 3 h), trimethylsilyl chloride (TMSCl) was added dropwise to the reaction mixture. The formation of organosamarium species as main intermediated of this electrochemical process was proposed. The products were isolated with good yields up to 75 %. To extend the scope of this approach, authors performed the homo-coupling of *N*-benzylideneaniline, which led to the corresponding diamine product with 48 % yield, as well as the cross-coupling of acetophenone and methyl acrylate [150]. Finally, it was found, that electrochemical reduction of CO_2 with benzyl halides in the presence of samarium(II) catalyst led to the corresponding carboxylation products [149].

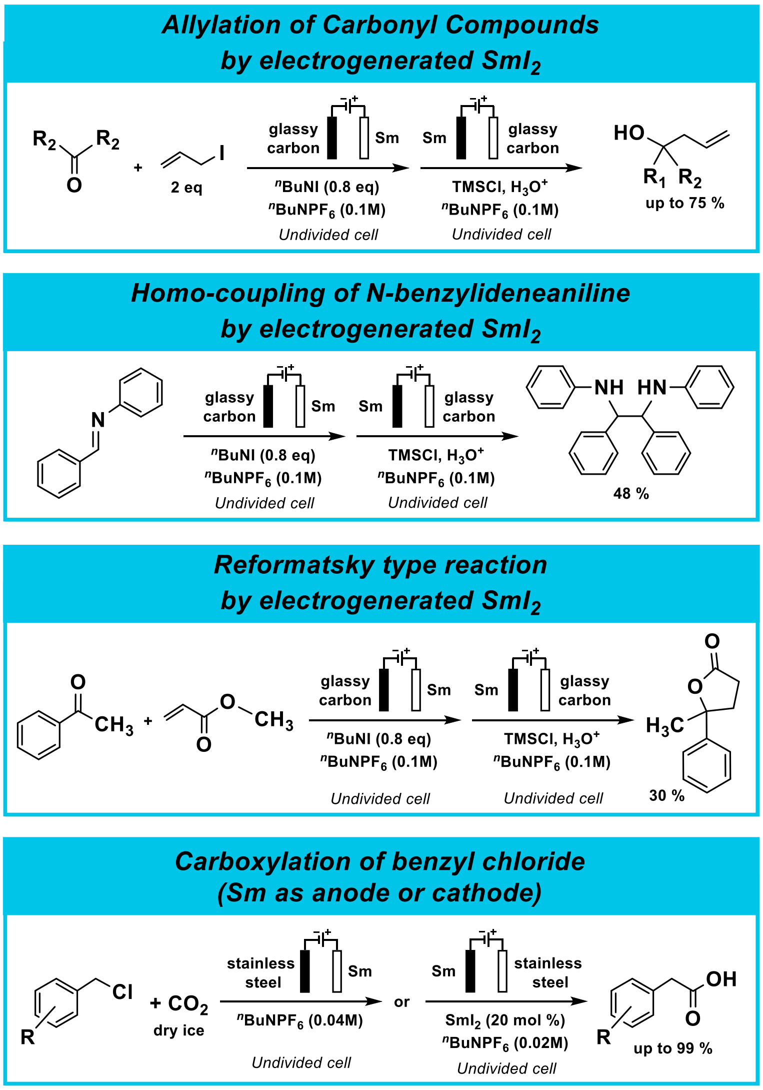


Figure 19. Examples of organosamarium-catalyzed electrochemical coupling reactions [149–151].

3.5. Organozinc-mediated electrochemical coupling reactions

Fillon and coauthors reported the electrochemical method for the generation of organozinc species and their *in situ* application in coupling reaction with acetyl chloride [152]. In this study, aromatic organozinc compounds were electrochemically generated from acetonitrile solution of aryl bromides in the presence of cobalt bromide as the catalyst in an undivided cell supplied with the sacrificial zinc anode and the stainless-steel cathode at the constant current (0.2 A). The obtained arylzinc reagents were coupled with acetyl chloride in the presence of palladium catalyst (Figure 20). A similar route to unsymmetrical biaryls *via* the electrochemical preparation of functionalized aromatic zinc organometallics in the presence of a nickel-complex as co-catalyst has been demonstrated by Sibille *et al.* [153].

Huang and Ren performed an electrochemical allylation of various carbonyl compounds, catalyzed by zinc (Figure 20) [154]. The authors used divided electrochemical cell, where a Nafion cation-exchange membrane separated cathodic and anodic compartments; the zinc cathode and the platinum anode were applied. The carbonyl compound and selected allyl bromides were added into the cathodic part and the constant current of 30 mA was passed through the resulting solution. The reaction is initiated by the reduction of allyl bromide on the zinc surface with the formation of allylzinc intermediate, which further undergo the interaction with aldehyde (or ketone) to give the final alcohol. The follow up process of the released Zn(II) species electroreduction to Zn(0) allows to regenerate zinc catalyst.

The formation of organozinc intermediates was also proposed in the electrosynthesis of Zn-based metal-organic frameworks [155]. The sacrificial process on the zinc anode was responsible for the generation of Zn^{2+} ions, meanwhile, the titanium cathode produced hydroxyl radicals from water. These radicals interacted with acrylamide in the presence of Ce^{4+} ions as an oxidant to form organozinc species, which react with acrylic acid leading to Zn-based (acrylamide-co-acrylic acid)

MOFs. The process performed in aqueous media in an undivided electrochemical cell under 10 A DC stabilized power (sulfate solution was used as the supporting electrolyte).

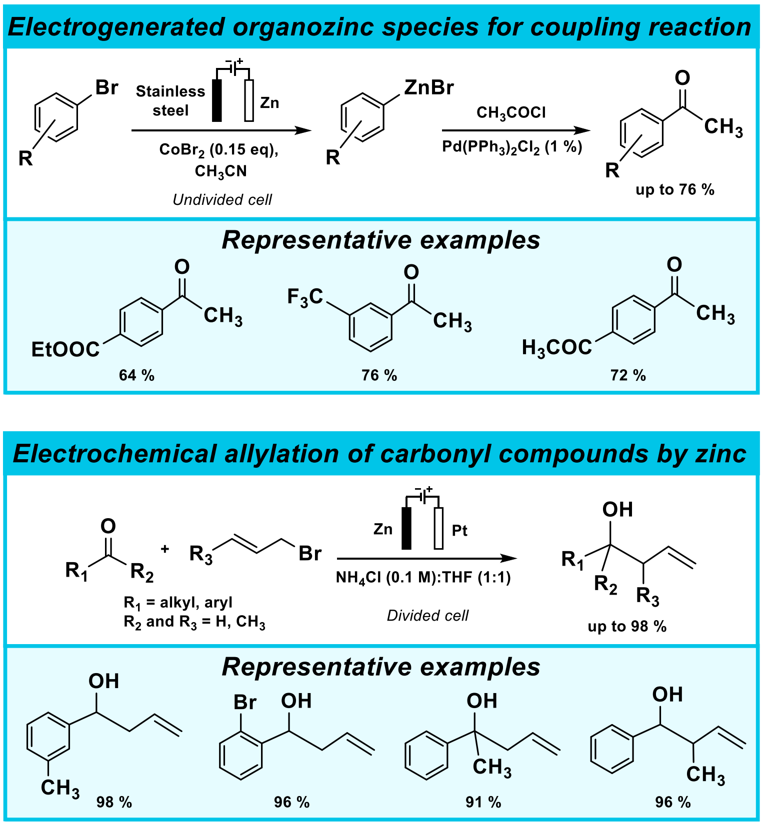


Figure 20. Representative examples of organozinc-catalyzed electrochemical synthesis of organic compounds [152,154].

3.6. Other examples

There are also organometallics based on other metals (like Cr, Mn, Fe, Co, Ru *etc.*) [156–163] are known to be applied *in situ* for different organic transformations. However such examples are rare, therefore, they are combined in this subchapter.

Thus, Durandetti *et al.* described the synthesis of various substituted benzhydrols by electrochemically induced intermediate formation of organochromium species [164,165]. In these investigations the electrochemical formation of organochromium reagents as catalysts was realized using a stainless steel (Fe/Cr/Ni = 72/18/10) sacrificial anode in DMF as the solvent in an undivided electrochemical cell under galvanostatic (0.3 A) conditions. This approach allows performing the electroreductive cross-coupling between benzaldehyde (or other aryl aldehydes) and aryl halides (Figure 21).

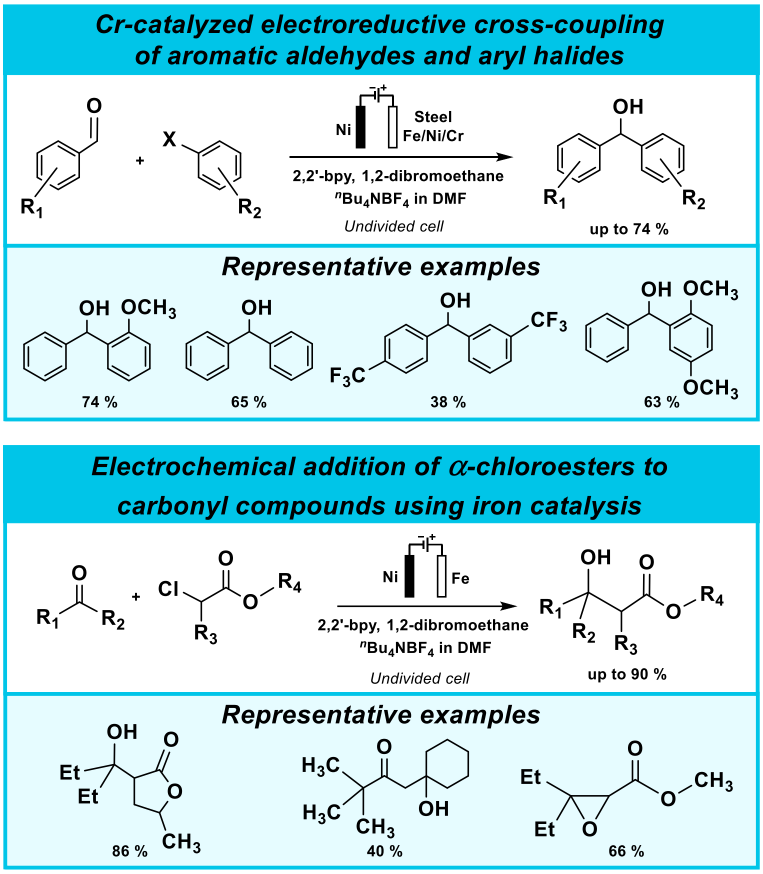


Figure 21. Representative examples of organoiron- and organochromium-catalyzed electrochemical synthesis of organic compounds [164,166].

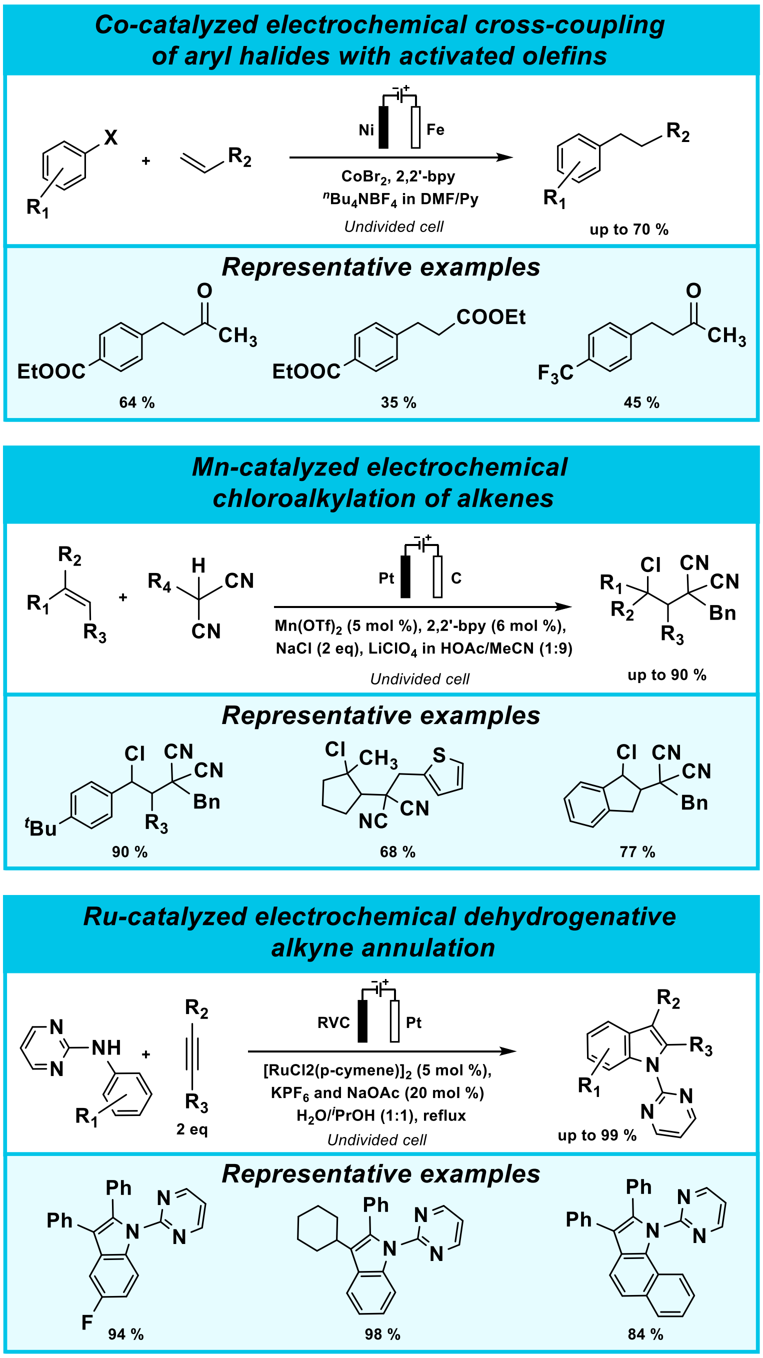
The same authors demonstrated the electrochemical iron-mediated reaction of *α*-chloroesters with carbonyl compounds (Figure 21) [166]. To perform this Reformatsky-type reaction, into an undivided electrochemical cell supplied with a nickel sponge as the cathode and an iron sacrificial anode, DMF solution of $^{n}Bu_4NBF_4$ (supporting electrolyte) and 1,2-dibromoethane was added. Afterward, 2,2′-bipyridine and selected carbonyl compound was added prior to *α*-chloroester. Then, constant current of 0.25 A was passed through the solution. Authors proposed the formation of $[Fe(II)Br_2(bpy)_3]$ complex, which is reduced to Fe(I) species at the nickel sponge and follow oxidative addition of these iron complexes to α-chloroesters generates organoiron derivatives.

Finally, *in situ* interaction of the formed organoiron complexes with carbonyl substrate produces the corresponding product (β-hydroxyesters or ketones). The formation of nitriles was also achieved by coupling of carbonyl compounds with α-chloronitriles.

Gosmini and coworkers developed the method for electroreductive coupling of aryl halides with activated olefins using $CoBr_2$/2,2'-bipyridine catalytic system (Figure 22) [167]. The electrolyses were conducted under galvanostatic (0.2 A) conditions in an undivided electrochemical cell with a sacrificial iron anode and nickel foam as a cathode. The electroreduction of starting cobalt salt in the presence of diimine ligand led to the formation of Co(I) species, which further interact with aryl halide and olefin to produce the coupling product vis formation of organocobalt intermediates. This method was successfully expanded to the coupling of unactivated alkenes [168]. Later, the authors demonstrated a possibility to obtain biaryl derivatives by the electrochemical cross-coupling of functionalized phenyl halides with 4-chloroquinolines in the presence of cobalt bromide under similar conditions [169]. The electrochemical properties of some formed arylcobalt complexes have been investigated using electrochemical methods (mainly by cyclic voltammetry, CV) [170,171].

Manganese-catalyzed electrochemical chloroalkylation of alkenes was recently shown by Lin *et al.* (Figure 22) [172]. Experiments were performed in an undivided cell supplied with a carbon felt anode and a platinum cathode under the constant current of 6 mA. According to the experimental data, proposed reaction mechanism includes Mn(III)-mediated Kharasch-type radical addition step. This method allows synthesizing a wide range of heterodifunctionalization products in high efficiency [173].

Recently a ruthenium-catalyzed electrochemical dehydrogenative alkyne annulation, which leads to indole derivatives, was reported (Figure 22) [174,175]. The electrolysis was conducted in an undivided electrochemical cell equipped with a RVC (reticulated vitreous carbon) anode and a platinum cathode under galvanostatic (0.13 mA) conditions, using aniline derivative, 2 equivs of diphenylacetylene under reflux conditions in the presence of catalytic amounts of KPF_6, NaOAc and $[RuCl_2(p\text{-cymene})]_2$. The postulated mechanism of this interaction includes the formation of organoruthenium intermediate.



Co-catalyzed electrochemical cross-coupling of aryl halides with activated olefins

Mn-catalyzed electrochemical chloroalkylation of alkenes

Ru-catalyzed electrochemical dehydrogenative alkyne annulation

Figure 22. Representative examples of organocobalt-, organomanganese and organoruthenium-catalyzed electrochemical synthesis of organic compounds [167,172,174].

4. Cyclic voltammetry and related methods in organometallic chemistry

4.1. A brief introduction

Cyclic voltammetry (CV) is perhaps the most powerful and available electroanalytical method for the investigation of the electrochemical properties and mechanisms of the redox processes of electroactive organometallic substrates. Its universality together with simplicity of the experiment has resulted in the extensive application of this method in different fields of chemistry [17,176–178]. Nowadays cyclic voltammetry has become a fundamental and even mandatory technique for analysis of both direct and indirect (mediated) electron transfer processes [179]. Thus, CV allows studying the redox properties of the substrate over a wide range of potentials [180]. The common setup of the electrochemical cell for conducting the CV measurements includes a working electrode, counter electrode, reference electrode, inert gas pipes and a magnetic stirrer (Figure 23) [181].

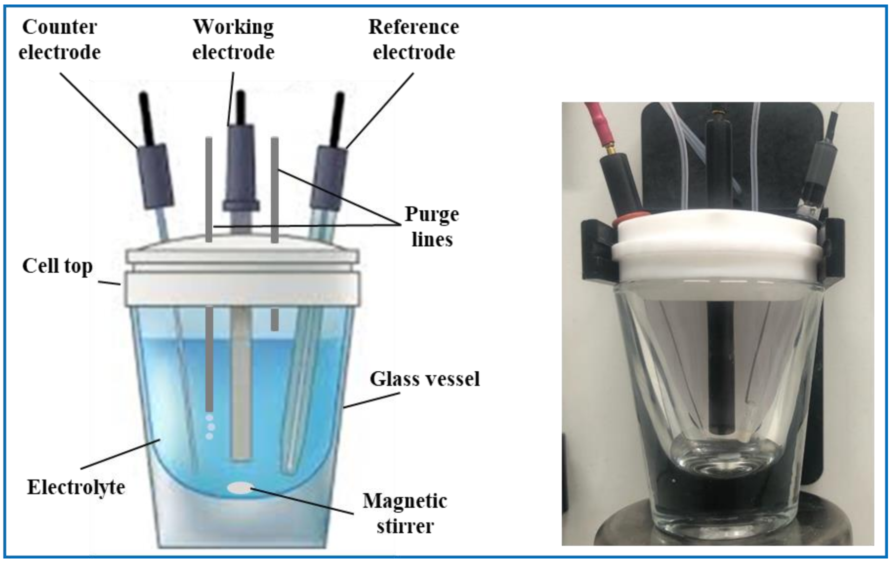


Figure 23. The typical electrochemical cell for CV experiments.

The used for electrochemical study potentiostat/galvanostat is being connected to the three-electrode system to control the voltage difference between the working and the reference electrodes. The role of the reference electrode is to measure the working electrode potential, while its own potential should be a constant (stable reference reaction occurs). The working electrode is responsible for the main electrochemical process, while counter electrode should pass the amount of current needed to balance the system (counter process occurs, which is usually not of the interest). The inert metal (such as gold or platinum) or a glassy carbon is usually used as a material of the WE [182]. The CE is typically made out of platinum, though carbon-based counter electrodes are also known [181,183].

Several reference electrodes are commonly used in aqueous electrochemical measurements. The examples include: the saturated calomel electrode (SCE), standard hydrogen electrode (SHE) and the silver/silver chloride electrode (Ag/AgCl) [184–186]. However, for the investigations of the electrochemical properties of organometallics the use of non-aqueous conditions are usually required. For the measurements, performed in organic media, the type of the reference electrode is not standardized [187]. Nevertheless, Ag^+/Ag couple is a very convenient reference electrode used for non-aqueous solvents [188,189]. However, according to the IUPAC recommendations, redox potentials measured using a non-aqueous reference electrode should be compared by adding an internal reference compound such as ferrocene [190–192]. Acetonitrile, dimethylformamide, dimethyl sulfoxide or some other solvents having high dielectric constants are typically applied for analysis of organometallic compounds by CV-method [193].

In a typical CV experiment, a cyclic potential sweep is applied to the working electrode, followed by the fixation of the current response. The potentiostat system sets the control parameters of the experiment to superimpose a cyclic potential sweep applied to the working electrode and displays the resulting current-potential curve, known as the cyclic voltammogram or CV-curve (Figure 24). The important information derived from the CV-curve is the peak potential (E_p) and the peak current (i_p), which are measured using peak parameter operations. There are three terms, which describe the rate of electron transfer processes between the WE and the substrate, namely, reversible (transfer proceed quickly), irreversible (slow transfer) and quasi-reversible (intermediate rates). The main conditions for reversible processes in cyclic voltammetry are the maintenance of the surface concentration of oxidized and reduced species at the values required by the Nernst equation [194]. The important criteria for a reversible process should be considered, namely [195,196] the difference between the potential of reduction (E_{pc}) and potential of oxidation (E_{pa}) is equal to $E_p = E_{pc}-E_{pa} = 0.058/n$ (n is the number of the electrons transferred), the ratio of the limiting cathodic and anode currents i_{pa}/i_{pc} should be equal to 1 (it should be noted, that this ratio does not depend on the scanning rate).

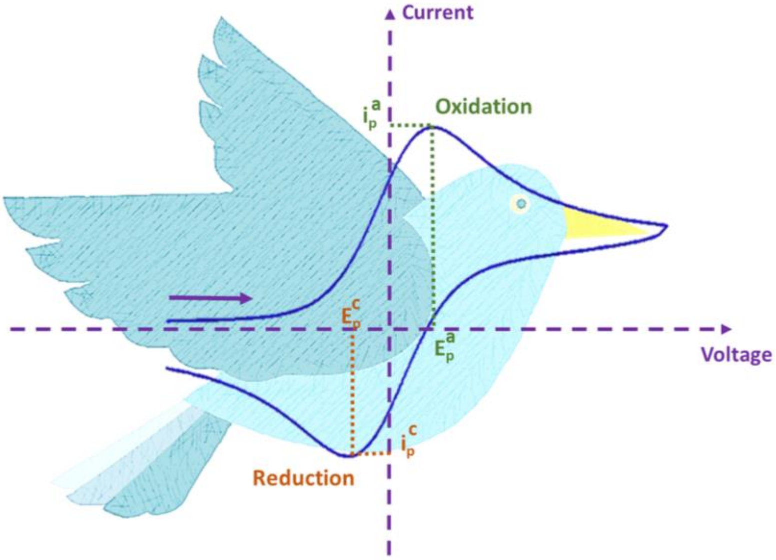


Figure 24. Schematic illustration of a typical cyclic voltammogram of a reversible electrochemical process.

4.2. Cyclic voltammetry of organometallic compounds

CV methods are indispensable in organometallic chemistry, since most of the metal complexes are electroactive substrates. Thus, an excellent review of William E. Geiger was devoted to the organotransition metal electrochemistry with emphasis on the CV application [65]. Moreover, to develop the electrochemical conditions leading to the formation of organometallic species (both direct electrosynthesis and *in situ* generation), the preliminary CV-investigations are mandatory to establish the required potentials and current density for a desired process [197,198].

Thus, to elaborate the procedure of the electrochemical synthesis of organonickel sigma-complexes of type [NiBr(Aryl)(bpy)], represented in Figure 13, the electrochemical behaviour of the starting [NiBr$_2$(bpy)] complex was studied in the presence of aromatic bromide using CV method (Figure 25) [52,98]. It was found, that the electroreduction of [NiBr$_2$(bpy)] in the absence of any substrate occurs in two successive, reversible electron-transfer steps, ascribed to the formation of Ni(0) complex (two-election peak C$_1$) and its further reduction to anion-radical species (one-electron response at C$_2$). Interestingly, the addition of aryl bromides led to a dramatic change in the morphology of the CV-curve with the disappearance of A$_1$ reoxidation peak and the formation of two new responds C$_3$ and C$_4$. These new peaks of the reductive processes were attributed to the reduction of a new compound, formed on the WE surface. Thus, performing the macroscale electroreduction of [NiBr$_2$(bpy)] complex in the presence of ArylBr was allowed to synthesize and to isolate organonickel sigma-complexes of type [NiBr(Aryl)(bpy)] (for the details of the electrosynthesis procedure see the section *2.2.5.*).

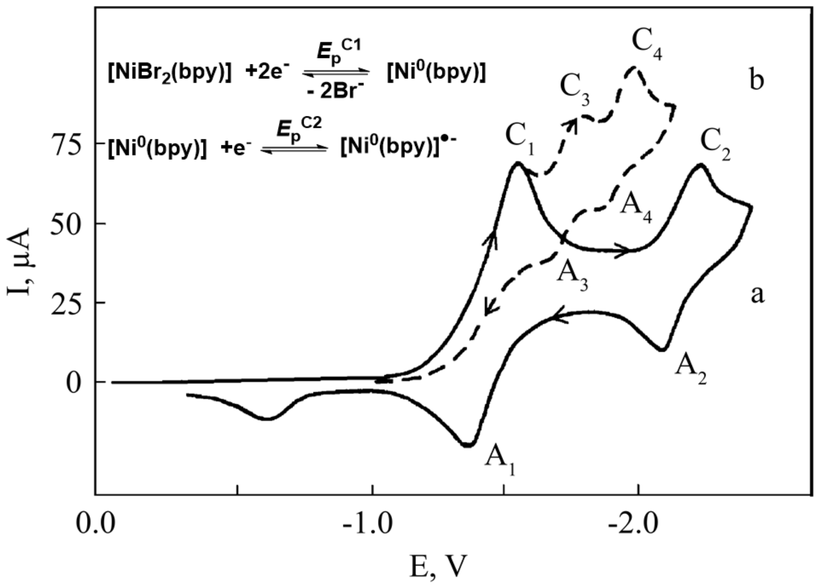


Figure 25. Cyclic voltammograms in DMF of [NiBr$_2$(bpy)] in the absence (a) and in the presence (b) of mesityl bromide (MesBr) [98].

The electrochemical properties of the formed [NiBr(Aryl)(bpy)] complexes were also investigated by CV techniques. Thus, an example of CV-curve, recorded for organonickel complex [NiBr(Mes)(bpy)], as well as the electrode processes ascribed to the corresponding peaks are demonstrated in Figure 26 [99,199]. It is interesting to note, that cathodic-anodic scanning of the WE potential led to the fixation of two reduction peaks C_1 and C_2 with anodic peaks of reoxidation A_1 and A_2, as well as oxidation peaks A_3 and A_4. While the reversible anodic-cathodic scanning allowed observation of a new reduction response C_3, which was ascribed to the reduction of $[Ni(Mes)(bpy)]^+$ cation, formed as a result of the anodic oxidation of the starting complex at A_4 potential (Figure 29). It has been found that anodic process at A_4 and cathodic reduction at C_1 lead to the coordinatively unsaturated organonickel species and can be considered as an "electrochemical activation" of such type complexes for using in catalysis and follow up chemical processes since the presence of a vacant coordination sites is a prerequisite for active form of transition metal catalysts in various catalytic processes [97,98,200,201].

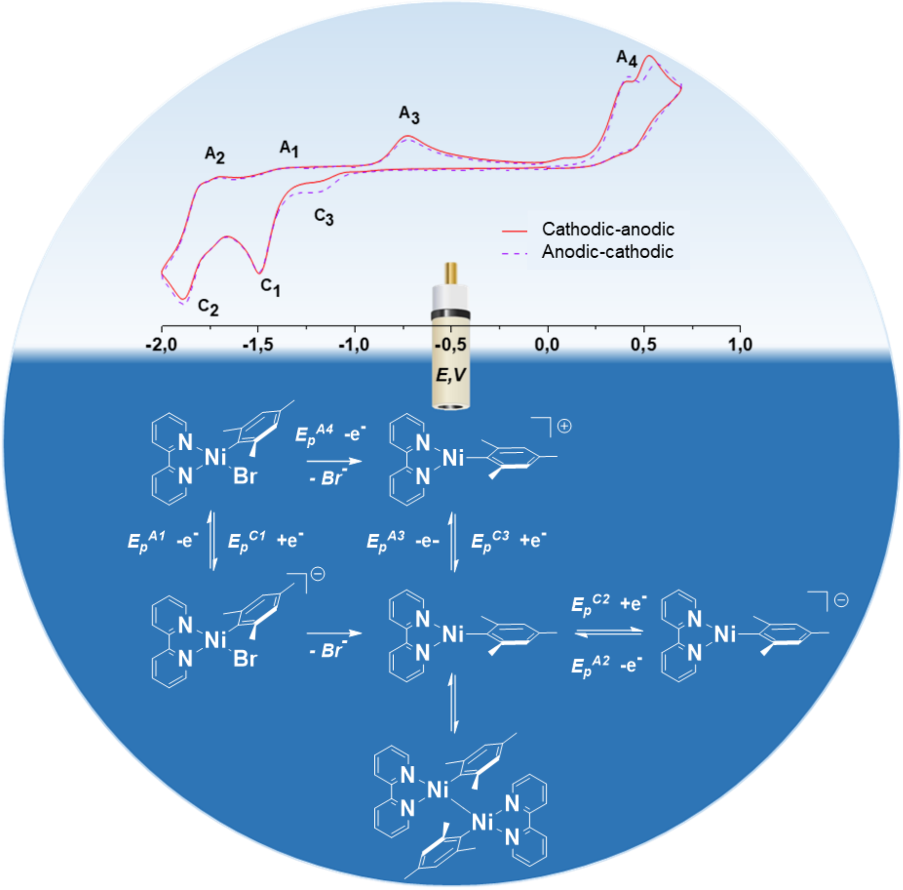


Figure 26. CV-curves recorded in DMF for organonickel complex [NiBr(Mes)(bpy)] and the scheme of the electrode processes ascribed to the corresponding peaks [99].

The application of CV methods allowed researchers to understand the mechanisms of a wide range of RedOx processes, including electron transfer to sandwich-type complexes of iron, cobalt, nickel, rhodium, ruthenium, *etc.* [202–211]; electroreduction of nickel dithiolenes [65], carborane complexes of different transition metals [212,213], arenechromium dicarbonylacetylene complexes [214]; electrooxidation of “triple-decker” compounds [215,216]; RedOx-induced structural changes in organometallics [65] *e.g.* in (η^6-naphthalene)tricarbonylchromium [217] and molybdenum bis-carbene complexes [218]; RedOx-induced reactivity changes in organometallic compounds [66] and many other examples. However, CV-curves are not always easy to interpret due to complexity of some patterns. The combination of cyclic voltammetry technique with spectroscopic methods [ultraviolet (UV)–visible, infrared (IR), electron paramagnetic resonance (EPR)] allowed getting additional structural information about the species formed on the electrode upon the redox process [219,220]. Thus, the method called *spectroelectrochemistry* (SEC) was elaborated and successfully applied as a powerful tool for the identification of conjugated or paramagnetic intermediates or other reaction products leading to a more complete analysis of electron-transfer processes and RedOx reactions in general [221,222].

As an example of the application of *in situ* EPR-SEC for identification and characterisation of the products formed in electrochemical process with participation of organometallic complexes we performed the investigation of the nature of the species formed by the electrooxidation of pyrazole-based PCN pincer complexes of nickel [(PCN)Ni^{II}X], where X = F, Cl, Br, I (Figure 27). The experiments were carried out in an electrochemical EPR cell supplied with a platinum WE, platinum CE and Ag/AgNO$_3$ RE. The electrochemical oxidation of the chloride and bromide complexes at A$_2$ peak potentials led to the fixation of EPR signal with g-factors 2.177 and 2.150

respectively. The hyperfine interaction (HFI) with splitting of 58 G was observed in the EPR spectrum of bromo-analogue with signal coupling coming from the ^{79}Br and ^{81}Br isotopes (I=3/2). This information allows concluding, that the complexes [(PCN)Ni^{II}Cl] and [(PCN)Ni^{II}Br] oxidize to give corresponding [(PCN)Ni^{III}X] derivatives. While the EPR spectra recorded for fluoride and iodide complexes upon their oxidation at A_2 peak values were identical with g-factor of 2.188 without resolved structure, which indicate the formation of halogen-free nickel(III) species (Figure 27-C) [223,224]. Similar results were obtained for PCN pincer nickel halides bearing a benzothiazole side-arm [225].

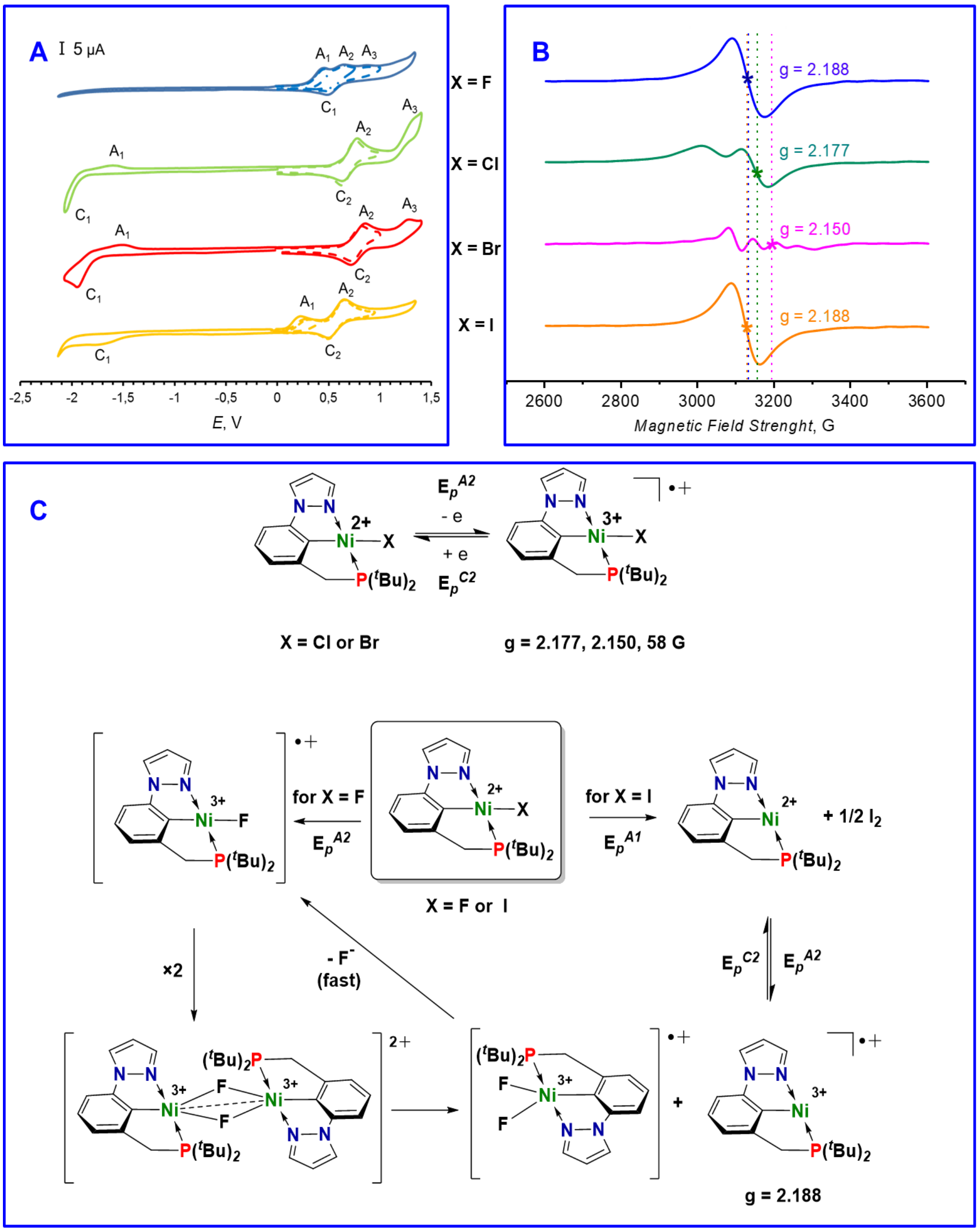


Figure 27. CV-curves (A), EPR spectra recorded upon the electrooxidation of [(PCN)NiX] (X=F, Cl, Br, I) complexes (B) and proposed electrochemical oxidation pathways [223].

5. Conclusions

In summary, the most useful and intriguing advances in organometallic electrochemistry with emphases on direct electrochemical synthesis of organometallics by formation of carbon—metal bond, *in situ* application of electrogenerated organometallic species for the synthesis of organic compounds, as well as cyclic voltammetry methods, applied for analysis of organometallic compounds, have been discussed in this review. The modern preparative electrochemical techniques allow obtaining organometallic compounds in high purity with high yields by different modes of electrolysis: galvanostatic conditions (applying a constant current density), potentiostatic conditions (maintaining a constant potential at the working electrode during the electrolysis); application of direct current (DC) or alternating current (AC); using the divided or the undivided electrochemical cells. The formed organometallic products may contain carbon—metal σ-bonds (*e.g.* cyano-, *N*-heterocyclic carbene or M—Aryl complexes) or π-bonds (*e.g.* cyclopentadienyl or allyl complexes). However, since such organometallic compound are highly reactive species, their isolation is not always possible. Nevertheless, application of such intermediates *in situ* allowed elaborating electrocatalytic methods for C—C bond formation reactions, involving a wide range of substrates. The application of spectroelectrochemical techniques (the combination of cyclic voltammetry with spectroscopic methods) allows to a precise analysis of the electron-transfer processes, leading to the better understanding of the mechanisms of the redox processes of the electrochemically substrates and organometallic species.

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Declaration of competing interest

The authors reported no potential conflict of interest.

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Conflict of Interest

Manuscript Title “Electrochemical methods for synthesis of organometallic compounds”

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Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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On behalf of the authors,
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